Rapid Ag/Sn/Ag transient liquid phase bonding for high-temperature power devices packaging by the assistance of ultrasound

Huakai Shao^a, Aiping Wu^{a,b,c}, Yudian Bao^a, Yue Zhao^{a,c}, Lei Liu^{a,b}, Guisheng Zou^{a,c}

^a Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China

^b State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

^c Key Laboratory for Advanced Materials Processing Technology, Ministry of Education, Beijing 100084, China

Abstract: Rapid transient liquid phase (TLP) bonding process on Ag/Sn/Ag system is achieved in air by the assistance of ultrasonic, which has great potential to be applied to high-temperature power devices packaging. In this study, the influence of ultrasonic effect on the morphology and growth kinetics of Ag₃Sn grains, and the joint microstructure, mechanical property and thermal reliability were systematically investigated. Experimental results indicated that the rapid consumption of the “dynamic” transient liquid phase was attributed to the accelerated dissolution of Ag substrate and the extrusion of liquid Sn, which were entirely induced by the complex sonochemical effects on the liquid/solid intermetallic compounds (IMCs) interface. An elongated scallop-like morphology of Ag₃Sn grains was developed during Ag/Sn interfacial reaction with ultrasonic, accompanied by widening of grooves between neighbored grains. This phenomenon is called as a strengthening thermal grooving, in which the grooves at grain boundaries provide stable molten channels for Ag atoms diffusion from the substrate. Consequently, the improved elemental diffusion was evaluated through the growth kinetics of Ag₃Sn IMCs, with conservative estimation of 6-16.5 times faster than the traditional TLP process. In addition, both excellent mechanical property and thermal reliability of the Ag-Sn intermetallic joint were experimentally verified by shear test and high-temperature storage test, respectively.

Key words: TLP bonding; ultrasonic; intermetallic compounds; growth kinetics; thermal grooving; reliability

1. Introduction

The demand for high-temperature electronic devices, with much higher thermal functionality and reliability, is continuously increasing in a wide variety of industries in recent years [1]. It has been reported that two important factors result in this trend. (1) The development of electronic component is tending towards miniaturization, high integration, multi-functionalization, and high power density. For example, as a result of the efforts to reduce the size of power control unit (PCU) in Toyota and increase its power output, the power density has increased by approximately 2.5 times from the first generation to the third generation [2]. (2) More and more electronic systems are required to be operated in harsh environments, such as high temperature, large current, and humid ambient. For instance, the control and sensing electronics in deep oil and gas drilling will be need to survive pressure reaching to 30000 psi and temperature up to 300 °C for deeper exploration [3]. The high-temperature applications bring great challenges to the electronic material and packaging technology. Nowadays, a wide band gap semiconductor technology has solved the problems of chip material in power devices, such as silicon carbide (SiC) and gallium nitride (GaN), which enable undergoing long-term operation at high temperatures of more than 300 °C. Therefore, the study of packaging methods is extremely crucial to promote the development of wide band gap semiconductors in power devices [4].

Presently, the transient liquid phase (TLP) bonding technology has emerged in the power electronics industry. In this process, an interlayer with low melting point (e.g. In, Sn) is utilized to react with high-melting-point substrates (e.g. Cu, Ag), such that produces a full intermetallic compounds (IMCs) joint at a relatively low temperature ($<300\text{ }^{\circ}\text{C}$). The TLP-bonded joints have much higher thermal reliabilities than the traditional soldered joints with Sn-based solders. However, the bonding process to obtain full IMCs is highly time-consuming ($>60\text{ min}$) due to its diffusion controlled reaction, which would lead to extra thermal stress and then decline the reliability [5-7]. Therefore, the development of a TLP process needing short time period is necessary, for not only the reliability of electronic devices but also the economically viable for mass production. Many reasonable studies have made considerable progress for this purpose. Soldering Cu/Sn/Cu sandwiches with the assistance of large electric current has been indicated extremely rapid formation of Cu_3Sn joint within several hundred milliseconds [8]. TLP sintering with Sn-coated Cu particles or Sn-Cu, Sn-Ag mixed powders has been demonstrated able to shorten the bonding time to a few minutes even several seconds [9, 10]. A 3-10 times faster TLP process has been achieved by using temperature gradient [11].

Recently, several other studies applying ultrasonic to assist TLP bonding process have also revealed rapid formation of full IMCs joint within several seconds [12-14]. Propagation of ultrasonic waves in a liquid medium will lead to complex sonochemical effects (e.g. acoustic cavitation and acoustic streaming) and dramatically affect the physical-chemical interactions at the solid/liquid interface [14-16]. As a result, the elemental diffusion in the liquid is greatly promoted, and both the morphology of intermetallic grains and the grain size of solder alloy are changed [17, 18]. Previous studies propose that the acoustic cavitation effect directly impacts on the surface of bare substrate, such that leads to a strong dissolution of the substrate into the melting interlayer; upon subsequent cooling process, the IMCs nuclei precipitate from the supersaturated liquid solder [4, 13, 14]. However, the IMCs may have formed before applying ultrasonic waves, especially for a faster reaction system, such as Ag/Sn couple. Under this condition, the acoustic cavitation effect will impact upon the liquid/IMCs interface, and the results or analyses may be different from the common explanations. Therefore, the mechanism of rapid consumption of the liquid layer should be further investigated in different systems. On the other hand, the accelerated degree of the elemental diffusion induced by the ultrasonic vibration has not been described with a quantitative analysis, of which corresponding influence on the growth of intermetallic grains adhere to the substrate is still unclear.

In the available literatures, the TLP bonding on the Ag-Sn binary system has been verified to be feasible for power devices operated at high temperatures. As studies report [19-21], the Ag_3Sn IMCs possess not only excellent thermal and electrical conductivities but also higher ductility than the other common intermetallic phases (e.g. Cu_6Sn_5 , Ni_3Sn) in electronics, which means a great potential to ensure the service performances of interconnections in harsh environments. Thereby in the case of Ag/Sn/Ag sandwiches, the purpose of this paper is to work toward the fast formation of a reliable intermetallic joint by the ultrasonic-assisted TLP bonding method. Three objectives would be achieved: (i) discussing the detailed process of the TLP bonding with ultrasonic under different conditions of bonding temperature and time; (ii) quantitatively analyzing the influence of ultrasonic effect on the morphology of the Ag_3Sn IMCs and the acceleration of elemental diffusion in the liquid; (iii) evaluating the room mechanical properties and thermal reliabilities of the full IMCs joints.

2. Experimental procedures

2.1. Material preparation

Two polished Cu rods with the dimension of 5.5 mm × 10 mm in diameter (bottom) and 5.5 mm × 6 mm in diameter (upper) were electroplated with 2 μm thick Ni layer followed by 25 μm thick Ag layer to be utilized as the substrate. Prior to bonding process, the faying surface of the substrate was ultrasonically cleaned in 5 vol. % HNO₃ solution for 10 min, subsequently rinsed with deionized water and anhydrous alcohol, and finally dried. A commercially pure Sn foil with 20 μm thickness (except for comparative experiments) was adopted as the interlayer, which was cut into 6 mm diametric disc. After cleaned in acetone for 5 min, the Sn foil was sandwiched between two Ag-plated Cu substrates.

2.2. Bonding process

Fig. 1(a) schematically illustrates the ultrasonic-assisted TLP bonding process. The samples were placed on the working platform and fixed by an aluminum-alloy fixture (fixture I shown in Fig. 1b). A constant bonding pressure of 0.5 MPa was applied (except for comparative experiments). High-frequency induction system equipped with temperature feedback control was used to heat the samples at ambient atmosphere, and a thermocouple was adopted to measure the real-time temperature of the bottom substrate. The temperature profile is illustrated in Fig. 1(c), in which the method-I was employed to accomplish the bonding process. It is necessary to explain that applying 1 s ultrasonic at 235 °C (pretreated temperature: 3 °C higher than the melting point of pure Sn, at 232 °C) is to remove the oxides on the faying surfaces of the substrates and improve the wettability of liquid Sn. The bonding temperatures were among 250, 280, 310, and 340 °C, and the bonding time (or ultrasonic time) was varied in a range of 2 to 15 s. An ultrasonic with 300 W (except for comparative experiments) in power and 20 kHz in frequency was applied during TLP process at bonding temperature.

Fig. 1. (a) Schematic diagram of the ultrasonic-assisted TLP bonding process; (b) illustration of two different fixtures for the Ag/Sn/Ag bonding process (fixture I) and the evaluation of Ag₃Sn growth kinetics (fixture II), respectively; and (c) heating schemes for the Ag/Sn/Ag bonding process (method I) and the evaluation of Ag₃Sn growth kinetics (method II)

2.3. Sample analysis

The bonded samples were mounted in epoxy resin, and then ground by 240, 600, 1000, 1500 and 2000 grade silicon carbide papers, subsequently polished by using diamond polishing agents. The microstructures of the joints were observed under a scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). In order to evaluate the mechanical properties, shear test was performed with a shear rate of 2 mm/min. Some typical fractures were analyzed by the SEM, EDS, and X-ray diffraction (XRD) technologies.

In addition, the 280 °C bonded Ag/Sn/Ag samples were then subjected to high-temperature storage

test in air, so as to uncover the thermal reliability of the full IMCs joint. The aging temperature is 350 °C, and the storage time is varied from 120 to 240 h. At last, the cross-sectional microstructures of the tested samples were investigated by an electro-probe micro-analyzer (EPMA).

2.4. Analysis of Ag₃Sn growth kinetics

For quantitatively assessing the influence of ultrasonic effect on the elemental diffusion, thickening kinetics of Ag₃Sn layer was carefully examined. A 25 µm-thick Sn foil mildly coated with rosin flux was placed on the Ag-plated Cu substrate, as depicted in Fig. 1(b). The samples were heated by following the temperature profile of method-II that shown in Fig. 1(c). The temperatures in bonding process were between 250 and 300 °C, and the bonding time was varied in the range of 5 to 120 s. An ultrasonic with 0, 300 and 500 W in power was applied during bonding process, respectively. After finishing the heating procedure, the bonded samples were immediately taken out from the fixture and cooled in air. Metallographic experiment was performed to measure the mean thickness of Ag₃Sn layer, in which the unreacted Sn was deeply etched by a 10 vol. % HNO₃ solution for 15 s. The mean thickness can be calculated by the equation as follow:

$$\theta = \frac{A}{L} \quad (1)$$

where A is the total area of the Ag₃Sn layer and L is the length of the coverage. In order to obtain the total area, the profile of Ag₃Sn layer was extracted by using an image analysis software, as shown in Fig. 2. At least seven different areas were employed to calculate the mean thickness of each sample.

Fig. 2. Illustration of extraction process on the Ag₃Sn layer profile

3. Results

3.1. Cross-sectional microstructure

Fig. 3(a)-(c) show the cross-sectional micrographs of the joints bonded at 250 °C for various time with 300 W ultrasonic. After 2 s, Ag₃Sn grains with scallop-like morphology formed at both the Ag/Sn interfaces, and a few Ag₃Sn particles were distributed within the residual Sn layer, as shown in Fig. 3(a). After 5 s (Fig. 3b), the Ag₃Sn grains on both sides impinged on each other, leading to the isolation of residual Sn into separate areas. Meanwhile, the spalling of Ag₃Sn grains was observed in the zone marked by white arrow marks, where some necks formed at the roots of the grains. After 15 s (Fig. 3c), the liquid layer was completely consumed, but accompanied by remaining a few pores in the “centerline” of the bonded joint. It is worth noting that the total thickness of the connection layer noticeably reduced with the increase in bonding time, which can be entirely attributed to the extrusion of molten Sn because of the “stirring” effect induced by acoustic streaming. An excessive liquid phase was squeezed out, despite promoting the consumption of transient liquid phase, which was also responsible for the formation of pores, through a similar mechanism described in other study [22].

Fig. 3(d)-(f) show the microstructures of the joints formed at different temperatures for 15 s with 300 W ultrasonic. All the full Ag_3Sn intermetallic joints could be obtained after a short period of bonding process, and they presented as much better mechanical integrities than the 250 °C bonded joint. More importantly, the thickness of the connection layer visibly increased with the increase in bonding temperature, about 7.12 μm , 11.65 μm , and 16.82 μm for the 280 °C, 310 °C, and 340 °C bonded samples, respectively, but wholly not exceeded the theoretical thickness of the Ag_3Sn layer (about 58 μm), which was calculated by the expression as follow:

$$t_{\text{Ag}_3\text{Sn}} = \frac{\rho_{\text{Sn}}}{\eta \rho_{\text{Ag}_3\text{Sn}}} t_{\text{Sn}} \quad (2)$$

where ρ_{Sn} and $\rho_{\text{Ag}_3\text{Sn}}$ are the densities of Sn and Ag_3Sn , at 7.28 and 9.39 g/cm^3 , respectively; η is the mass proportion of Sn in Ag_3Sn , at 26.83%; and t_{Sn} is the thickness of Sn foil, at 20 μm . This phenomenon has never been observed in the conventional TLP bonding process.

Fig. 3. Cross-sectional microstructures of the joint bonded at different temperature for various time with 300 W ultrasonic and 0.5 MPa bonding pressure: 250 °C for (a) 2 s, (b) 5 s (the unreacted Sn was deeply etched by an etching solution), and (c) 15 s; (d) 280 °C, (e) 310 °C, and (f) 340 °C for 15 s

A series of comparative experiments were conducted in order to further investigate the mechanism of the ultrasonic-assisted TLP bonding process. Fig. 4a shows the micrograph of the joint bonded at 250 °C for 15 s without ultrasonic. A thin layer of scallop-like Ag_3Sn formed at both the upper and the bottom interfaces, and nearly 19 μm thick Sn layer remained in the joint. Our previous study indicated that more than 120 min time duration was required to accomplish the TLP process even though bonding at 280 °C. Obviously, applying an ultrasonic dramatically shorten the bonding time. And further, Fig. 4b shows the micrograph of the 50 μm Sn foil bonded sample. A full IMCs joint could be also obtained within 15 s, but it was composed of a relatively thicker Ag_3Sn layer in comparison to the corresponding joint formed with 20 μm Sn foil (Fig. 3c). Similarly, a great amount of liquid Sn was squeezed out by the ultrasonic vibration. For insuring the mechanical integrities, it is very important to control the amount of the squeezed-out Sn by choosing appropriate ultrasonic power and bonding pressure. Otherwise, as shown in Fig. 4(c), the joint bonded with 500 W ultrasonic and 5 MPa bonding pressure revealed that a continuous defect of gaps occurred in the bonded layer.

From the above observations, it can be concluded that the greatest advantage of the ultrasonic-assisted TLP bonding is the ultra-rapid formation of full IMCs joint. Two important factors might be responsible for this result. On the one hand, the ultrasonic effect accelerated the elemental diffusion in the liquid. Propagation of ultrasonic waves in a liquid medium can generate acoustic cavitation phenomenon [13-16], which includes the formation, growth, and rapid implosive collapse of

vapor filled micro-bubbles. Rapid bubble implosion can induce tiny “hot spot” with the localized temperature and pressure estimated to be about 5000 K and 0.1 GPa, respectively [23, 24]. Extra energy input induced by hot spots promotes the Ag atom diffusion in the molten Sn. Moreover, ultrasonic waves can generate intense acoustic streaming like “stir” in the liquid, which could also accelerate the diffusion rate of Ag atoms [14]. On the other hand, the ultrasonic vibration directly led to the extrusion of molten Sn, thereby the liquid layer can be regarded as a “dynamic” transient liquid phase, with a gradual reduction in its thickness during bonding process. The detailed mechanism will be further studied in the following.

Fig. 4. Cross-sectional microstructures of the joints bonded at (a) 250 °C for 15s without ultrasonic and with 0.5 MPa bonding pressure (the unreacted Sn was deeply etched by an etching solution); (b) 250 °C for 15s with 300 W ultrasonic, 0.5 MPa bonding pressure, and 50 μm Sn foil; and (c) 250 °C for 15s with 500 W ultrasonic and 5 MPa bonding pressure

3.2. Morphology and growth kinetics of the Ag₃Sn IMCs

The influence of ultrasonic effect on the morphology of Ag₃Sn grains was investigated with different ultrasonic power, bonding time, and temperature. As shown in Fig. 5 (a)-(c), the classical scallop-like morphology of the Ag₃Sn grains was developed at the Ag/Sn interface for the samples treated at 250 °C without ultrasonic. While the Ag₃Sn grains formed with 500 W ultrasonic were characterized by a more elongated shape in the growth direction, with much wider grooves between two neighboring grains and sharp corners on the top of grains (Fig. 5d-f). The IMC layer formed in the higher-power ultrasonic treatment (500 W, Fig. 5f) was relatively thicker than that in the lower-power ultrasonic process (300 W, Fig. 5g). An increase in groove width was also captured in higher temperature bonding process with ultrasonic, as shown in Fig. 5 (h)-(i). Furthermore, some abnormally large Ag₃Sn grains with irregular shapes were observed at the Ag/Sn interface treated at 300 °C with 500 W ultrasonic (Fig. 5i). The mean thickness of the Ag₃Sn layer increased with the increase in not only the ultrasonic power but also the bonding time and temperature. It is worth noting that widening of the grooves is a particular event, and it may be responsible for the elongated morphology and the abnormal growth of Ag₃Sn IMCs by promoting the dissolution of Ag substrate. This will be discussed in the section 4.1 in detail.

In this study, the quantitative analysis of the accelerated elemental diffusion was described by the growth kinetics of the Ag₃Sn IMCs. Many studies have reported that thickening kinetics of an IMC layer follow a power law model of [5, 6, 25-27]:

$$\theta = kt^{1/n} \quad (3)$$

where θ is the mean thickness of the IMC layer; k is a growth constant related to the diffusion rate; and n is a time exponent. Values for the time exponent enable the determination of the possibly dominant mechanisms responsible for the IMCs evolution [25, 26]: (i) $n=1$ means a reaction-controlled process; (ii) $n>1$ means a diffusion-controlled process. Especially, the exponent of $n=2$ indicates that the kinetics are controlled by volume diffusion, while $n=3$ represents that the IMCs growth are controlled by grain boundary diffusion accompanied by grain coarsening.

In addition, the growth constant can be expressed by the following Arrhenius relationship [27]:

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (4)$$

where k_0 is the intrinsic growth constant for a given diffusion couple; Q is the activation energy for the IMCs thickening process; R is the gas constant (8.314 J/mol); and T is the bonding temperature.

Fig. 5. Morphologies of typical Ag_3Sn grains formed with or without ultrasonic: (a) 0 W-250 °C-5 s; (b) 0 W-250 °C-60 s; (c) 0 W-250 °C-120 s; (d) 500 W-250 °C-5 s; (e) 500 W-250 °C-60 s; (f) 500 W-250 °C-120 s; (g) 300 W-250 °C-120 s; (h) 0 W-300 °C-120 s; and (i) 500 W-300 °C-120 s

In the available literatures, it has always been assumed that volume diffusion is the dominant process controlling the formation and evolution of IMCs at temperatures below or above the melting point of solder [25]. A time dependence of the form $t^{1/n}$ with $n \geq 3$ is also developed for the thickening growth of IMCs, which is explained by a model of grain boundary/molten channel-controlled process [5, 28]. In this study, both the $n=2$ and 3 were adopted to investigate the influence of ultrasonic effect on the Ag_3Sn thickening kinetics by regression analysis of experimental data. Fig. 6 shows the plot of mean thickness of Ag_3Sn layer formed with ultrasonic. The analysis indicated that the time exponent of $n=3$ could be preferably consistent with the measured data, thus Ag_3Sn growth was mainly controlled by grain boundary/molten channel diffusion mechanism, following the study of Li et al. [5].

Fig. 6. Thickening kinetics of Ag_3Sn IMCs formed with ultrasonic: (a) $t^{1/2}$ and (b) $t^{1/3}$ form fit

The detailed results on the Ag_3Sn thickening kinetics were summarized in table 1. The acceleration of Ag atom diffusion induced by the ultrasonic effect was approximately evaluated by using the growth constants, and it was estimated to be 6-16.5 times faster than the traditional TLP bonding process, depending on the ultrasonic power and temperature. This estimation was a

conservative result, because a stronger attenuation of ultrasonic existed in the process of Ag/Sn interfacial reaction, as depicted in Fig. 1(b) (fixture II). Even so, the improved degree of the elemental diffusion was not sufficient to make the transient liquid phase be completely consumed within several seconds. Therefore, the “dynamic” liquid layer caused by the extrusion of molten Sn should not be neglected to discuss the rapid formation of full IMCs joint.

Table 1 Summary of growth constants in Ag₃Sn thickening kinetics

Power (W)	Temperature (°C)	Growth constant k ($\mu\text{m}^3/\text{s}$)
0	250	0.69 [5]
300	250	4.17
500	250	6.61
0	300	1.763 [5]
500	300	29.1

3.3. Mechanical properties of the full IMCs joints

Fig. 7 shows the mechanical properties of the full Ag₃Sn joints as a function of bonding temperature. The shear strength firstly increased but lastly decreased with the increase in bonding temperature, with a highest value of 53.7 MPa at temperatures in the range of 280 to 310 °C. The relatively lower shear strength of the joint formed at 250 °C is associated with the pores in the bonded layer, while the decline of the measured value at 340 °C may be attributed to the increase in grain size, since the growth kinetics of IMCs strongly depends on temperature.

Fig. 7. Variation in joint shear strengths with bonding temperature, where the Ag/Sn (20 μm)/Ag sandwich samples were bonded at different temperatures for 15 s with 300 W ultrasonic and 0.5 MPa bonding pressure

Fig. 8(a)-(b) show the typical fracture surfaces of the full Ag₃Sn joints formed at 280 °C and 340 °C. EDS analyses indicated that both the fractures propagated inside the Ag₃Sn layer. In the 280 °C bonded joint (Fig. 8a), shear bands almost extended throughout the fracture surface, indicating a relatively ductile feature. However, a great amount of cleavage steps were generated on the fracture surface of 340 °C bonded sample (Fig. 8b), indicating a reduction of the ductility. Based on the observations in Fig. 5, it is believed that the coarsening of Ag₃Sn grains with increasing temperature may be responsible for this distinct change. Furthermore, the XRD analysis showed that no residual Sn was detected on the fracture surfaces (Fig. 8c), which demonstrated that full Ag₃Sn IMCs joints indeed formed within an extremely short time period.

Fig. 8. Fracture surfaces of the Ag/Sn/Ag TLP joints formed at (a) 280 °C and (b) 340 °C for 15 s with 300 W ultrasonic and 0.5 MPa bonding pressure; and (c) XRD analysis of the consisting phases on the fracture surfaces

3.4. Thermal reliabilities of the full IMCs joints

Fig. 9 shows the cross-sectional SEM images and the corresponding elemental distributions of the high-temperature tested joints aged at 350 °C for various time. After 120 h (Fig. 9a), the Sn atoms had been distributed across the entire Ag layer, resulting in the complete transformation from Ag_3Sn and Ag matrix to $\text{Ag}(\text{Sn})$ solid solution, identified by the EPMA analysis (table 2). Meanwhile, a large number of irregular $(\text{Ag}, \text{Ni})_3\text{Sn}$ intermetallic particles orderly dispersed adjacent to both the Cu/Ag(Sn) interfaces, with about 4 μm distance to the interface. With a longer storage time of 240 h (Fig. 9b), a similar microstructure of $\text{Ag}(\text{Sn})$ solid solution was observed in the joint, while $(\text{Ag}, \text{Ni})_3\text{Sn}$ particles with more Ni-content and larger size mainly dispersed close to both the Cu/Ag(Sn) interfaces, and they were also randomly distributed within the central zone of the $\text{Ag}(\text{Sn})$ solid solution layer. This indicates that Ni atoms diffused into the bonded layer from the Ag/Ni interface during aging test. As shown in table 2, a slightly change of the Cu-content within the connection layer indicated the diffusion barrier effect of Ni layer between Cu and Ag. The formation of Ag-Ni-Sn intermetallic phase and the increase of Ni-content in the particles with aging time are wholly ascribed to the lower formation enthalpy of Ni-Sn IMCs (Ni_3Sn_4 : -7.4 kJ/mol_{Sn}; Ni_3Sn_2 : -17.5 kJ/mol_{Sn}; and Ni_3Sn : -21kJ/mol_{Sn} [29]) in comparison to the Ag_3Sn with -4.2 kJ/mol_{Sn} [30].

Fig. 9. EPMA mapping images of the high-temperature tested joints (280 °C bonded samples) after aging at 350 °C for (a) 120 h and (b) 240 h

Table 2 Phase identification in Fig. 9 by the EPMA analysis

Marked zone		A	B	C	D
Composition	Ag	96.5425	29.7094	95.1261	16.0036
(at. %)	Sn	2.8138	30.1201	3.6415	24.3987

	Ni	-	35.7437	0.0113	54.8722
	Cu	0.6437	4.4268	1.2211	4.7255
Phase	Ag(Sn)	(Ag, Ni) ₃ Sn	Ag(Sn)	(Ag, Ni) ₃ Sn	

With storage time increasing from 120 to 240 h, as shown in Fig. 9, similar microstructures were observed in the joints, and there were no heat cracks or any other defects within the connection layer. This reveals an excellent thermal reliability of the joint. In addition, table 3 summarized the thermal, electrical, and mechanical properties of typical Cu-Sn IMCs and common solders for comparison. Higher thermal conductivity and lower electrical resistivity enable the interconnection to exhibit better performance in heat dissipation and electrical signal transmission, respectively. From table 3, the Ag₃Sn IMCs possess excellent performance in terms of thermal and electrical conductivities, and mechanical properties. It is believed that the ultrasonic-assisted TLP bonding process with Ag/Sn/Ag sandwiches has high potential to be applied in the packaging of next generation power devices, such as SiC and GaN.

Table 3 Comparison of thermal, electrical, and mechanical properties of the Ag₃Sn with typical Cu-Sn IMCs and Sn-based solders in electronics [20, 21, 31-36]

Phase	Thermal Conductivity (W/(m·K))	Re-melting Point (°C)	Coefficient of Thermal Expansion (ppm/°C)	Electrical Resistivity (μΩ·cm)	Young's Modulus (GPa)	Hardness (GPa)	Fracture Toughness (MPa/m ^{1/2})
Ag ₃ Sn	44.8	480	18.2	6.08	78.9	3.25	*
Cu ₆ Sn ₅	34.1	415	17.2	17.5	112.3	6.38	2.8
Cu ₃ Sn	70.4	676	14.8	8.8	134.2	6.12	5.7
Sn _{3.5} Ag	78	221	30	12.3	51.3	0.27	-
Pure Sn	63.2	232	23	11.5	46.9	0.22	45

* The fracture toughness of Ag₃Sn is very difficult to be determined by the nano-indentation measurement due to no induced cracks formation, but there is no doubt that the Ag₃Sn have relatively excellent ductility compared with the Cu-Sn IMCs [36].

4. Discussion

4.1. Strengthening thermal grooving at Ag₃Sn grain boundaries

In fact, the IMCs growth can be regarded as a dynamic equilibrium process, because a dissolution behavior of IMCs occurs from both grain boundaries and grain surfaces in contact with the liquid, which affects not only the IMCs growth kinetics but also their morphologies [37-39]. Moreover, the dissolution process is prone to happen at the grain boundaries due to their high interfacial energies. This phenomenon is known as thermal grooving effect. In the process of grooving, atomic migration by preferential dissolution of IMCs from the regions of boundary intersections is likely to force the groove to deepen, resulting in a molten channel penetrating into the grain boundaries [37]. It has been reported that the stability of molten channel during bonding is crucial for the growth of the IMC layer [40].

The thermal grooving was also observed in this study. Fig. 10(a) shows an initially planar Ag₃Sn layer with average thickness of 14 μm which was formed by solid-state aging of Ag/Sn samples at 150 °C for 10 days. The annealed samples were then subjected to reflow soldering at 250 °C for various time with or without ultrasonic. After soldering for 15 min without ultrasonic (Fig. 10b), relatively shallow grooves formed at Ag₃Sn grain boundaries, resulting in the scalloped structure of the top surfaces of the grains, and the dihedral angle (φ) of the grooves became smaller than the initial state. It was proposed that the formation of grooves or scalloped grains is the result of IMCs dissolution during solid-liquid interfacial reaction. In the 30 s soldered sample processed with 300 W ultrasonic (Fig. 10c),

the grooves almost penetrated into the Ag_3Sn layer, accompanied by serious necking down at the roots of Ag_3Sn grains, and an elongated morphology of the intermetallic grains was developed, moreover, the IMCs locating below thermal grooves extended to the Ag substrate (marked by a yellow ellipse). This phenomenon reveals that the grooves can provide fast channels for Ag atoms diffusion from the substrate, and further promote the dissolution of the Ag substrate and then accelerate the vertical growth of the Ag_3Sn grains. In the 30 s soldered sample processed with 500 W ultrasonic (Fig. 10d), a great amount of Ag_3Sn particles detached from the Ag substrate and were distributed within the liquid Sn, presenting as rod-like or spherical structure, and their sizes were smaller but quantities were larger than those in the process with 300 W ultrasonic. Necking down at the roots of Ag_3Sn grains was also observed, and it was responsible for the detachment of Ag_3Sn particles from the Ag substrate.

Fig. 10. Thermal grooving at Ag_3Sn grain boundaries in the annealed Ag/Sn samples: (a) the as-aged sample formed upon annealing at 150 °C for 10 days; soldering at 250 °C for (b) 15 min without ultrasonic, (c) 30 s with 300 W ultrasonic, and (d) 30 s with 500 W ultrasonic

Under the effect of ultrasonic, stable grooves can be generated within an extremely short time (< 30 s), and their widths, depths and quantities are significantly increased in comparison to the soldering process without ultrasonic. We call this phenomenon as a strengthening thermal grooving, which can be ascribed to the effect of acoustic cavitation on the dissolution behavior of the Ag_3Sn IMCs. Specifically, the collapse of the surrounding bubbles leads to the emission of shock waves with a pressure of several GPa and a starting shock velocity of ~4000 m/s [16]. Furthermore, the “micro-jet” phenomenon in water has been captured by the study of Ref [41]. The liquid micro-jets, shock waves, and localized high temperature directly impacted on the surfaces of Ag_3Sn grains, because the IMCs had formed during the heating process. This impact could accelerate the dissolution rate of the Ag_3Sn from the regions at grain boundaries. With continuing ultrasonic propagation, the strengthening thermal grooving was generated at Ag_3Sn grain boundaries, like a chain reaction process, leading to the formation of stable molten channels. Fig. 11 schematically illustrates the strengthening grooving process with ultrasonic.

Fig. 11. Schematic diagram of the strengthening thermal grooving at IMCs grain boundaries (not to scale): (a) before ultrasonic

The deepening and widening of the grooves results in an increase in the curvature of the grain boundaries, which leads to an increase in the equilibrium concentration of the adjacent melt as indicated by the equation [37]:

$$\frac{C_\rho - C_0}{C_0} = \alpha \rho \frac{\gamma_{il} \Omega}{k_B T} \quad (6)$$

where C_ρ is the liquid composition in equilibrium with a surface with curvature ρ ; C_0 is the liquid composition in equilibrium with a planar surface; $\alpha = (1 - C_0)/(C_0 - C_i)$, C_i is the composition of the IMCs; γ_{il} is the IMCs/liquid interfacial energy; Ω is the molecular volume of the IMCs; and k_B is the Boltzmann constant. The Eq. (6) reveals that the solubility of Ag in the melt is enhanced with increasing grain boundary curvature. Following Dybkov's analysis [42], the dissolution rate of a solid in liquid can be expressed by the equation:

$$\frac{dC}{dt} = k^* \frac{S}{V} (C_s - C) \quad (7)$$

where k^* is the dissolution rate constant; S is the surface area of the IMCs contacting with the molten solder; V is the volume of the molten solder; C_s is the solubility of Ag in the molten solder at bonding temperature. The Eq. (7) indicates that the dissolution rate of Ag substrate is proportional to the difference between the concentration of the liquid and the solubility of Ag at the bonding temperature.

From Eq. (6) and Eq. (7), the dissolution rate of Ag substrate was accelerated through the widening grooves, or molten channels. In addition, acoustic streaming could also improve the dissolution process of the Ag substrate into the liquid by promoting Ag atoms diffusion. According to the flux-driven ripening (FDR) theory [40], the growth of Ag_3Sn grains in the normal direction is promoted by the increase in Ag flux from the substrate, as illustrated in Fig. 11, which enable to explain the elongated morphology of Ag_3Sn grains. Furthermore, it is believed that the strengthening thermal grooving is responsible for the spalling of Ag_3Sn grains (Fig. 3b) and the rapid formation of full Ag_3Sn joints.

4.2. Mechanism of the ultrasonic-assisted TLP bonding process

A schematic drawing for the proposed mechanism of the ultrasonic-assisted TLP bonding process is presented in Fig. 12. The traditional low-temperature TLP bonding process is also discussed, and it can be divided into three stages [22, 43]: (i) heating to the targeted bonding temperature (e.g. 300 °C), accompanied by solid-state diffusions; (ii) isothermal solidification at the front interface between the solid IMCs and the liquid, in which the prior IMCs can act as a diffusion “barrier” layer for the dissolution of the substrate, leading to a highly time-consuming characteristic in the TLP process; (iii) homogenization within the connection layer to form anticipated microstructures, for example, the transition process from Cu_6Sn_5 into Cu_3Sn in Cu-Sn TLP system.

Fig. 12. Model of the ultrasonic-assisted TLP bonding process: (a) heating to the pretreated temperature; (b) removing the oxides locating at liquid/substrate interface at pretreated temperature; (c) ultra-rapid isothermal solidification of the “dynamic” transient liquid phase at bonding temperature

Based on the above analyses, the ultrasonic-assisted TLP bonding process is divided into three stages, which is detailed as follow:

- (i) Heating to the pretreated temperature (slightly higher than the melting point of the interlayer). In this process, both the substrate and the interlayer will be oxidized by air.
- (ii) Removing the oxides locating at the liquid/substrate interface by acoustic cavitation effect. In the literatures, it is reported that the acoustic cavitation effects can “microdamage” the solid surface, which is known as cavitation erosion [14, 16]. During applying 1 s ultrasonic at the pretreated temperature, the collapse of surrounding bubbles close to the substrate directly impacts on the solid surface, leading to the detachment of thin oxide films from the substrate. Moreover, the intense acoustic streaming will expel the oxide impurities from the liquid layer due to the bad wetting of the liquid on them.
- (iii) Ultra-rapid isothermal solidification of the “dynamic” transient liquid phase at bonding temperature. The “dynamic” represents a gradual reduction in the liquid layer, as the molten Sn is squeezed out by ultrasonic vibration. Furthermore, the strengthening thermal grooving effect promote the dissolution of the substrate by accelerating the diffusion of Ag atoms through the paths of stable molten channels. In this way, an extremely fast growth of the IMCs is achieved, and the two important factors are beneficial to the rapid consumption of the liquid.

4.3. Increase of the connection layer thickness with bonding temperature

As mentioned above, the thickness of connection layer in full Ag_3Sn joints increased with the increase in bonding temperature. Fig. 13 shows the measured values that strongly depend on bonding temperature. This study proposes that the reasons for this finding are the extrusion of liquid Sn by ultrasonic vibration and the growth kinetics of IMCs depending on temperature. It is believed that more liquid is squeezed out by the “stirring” effect of acoustic streaming during TLP process at lower temperatures, due to a relatively slower growth rate of the IMCs.

Fig. 13. Variation in the thickness of connection layer with bonding temperature

According to the growing process of IMCs, the total Ag_3Sn layer formed at temperature T in TLP bonding is composed by two parts: during the heating stage (due to relatively slower heating rate in the bonding process) and the TLP process at bonding temperature. From the Eq. (3) and Eq. (4), the first part can be expressed by the following differential equation:

$$d\theta_H = k_1 \exp\left(-\frac{Q}{R(T_0 + dT)}\right) \left(\frac{T - T_0}{\dot{T}}\right)^{\frac{1}{n_1}} (8)$$

where θ_H is the mean thickness of the IMCs formed during heating stage; k_1 is the intrinsic growth constant related to the given diffusion couple; T_0 is the pretreated temperature (235 °C); $\dot{T}$ is the heating rate (15 K/min); and n_1 is the time exponent at earlier stage without ultrasonic. This formula is a complex differential equation, such that is very difficult to solve and express by a general equation. Therefore, the Eq. (8) was simplified by:

$$\theta_H \approx k_1 \exp\left(-\frac{Q}{R(T_0 + \Delta T)}\right) \left(\frac{\Delta T}{\dot{T}}\right)^{\frac{1}{n_1}} = k_1 \exp\left(-\frac{Q}{RT}\right) \left(\frac{\Delta T}{\dot{T}}\right)^{\frac{1}{n_1}} (9)$$

where $\Delta T = T - T_0$. This equation indicates that the mean thickness of the IMC layer formed during heating stage is as an exponent function of bonding temperature. The second part can be expressed by the following equation:

$$\theta_T \approx k_2 \exp\left(-\frac{Q}{RT}\right) (t_T)^{\frac{1}{n_2}} (10)$$

where k_2 is the intrinsic growth constant related to the ultrasonic parameters; t_T is the ultrasonic bonding time (15 s); and n_2 is the time exponent for the interfacial reaction with ultrasonic. The Eq. (9) and Eq. (10) indicate a complex exponent relationship between the connection layer thickness and bonding temperature. The fitting plot for the experimental data is in good agreement with the theoretical model, as shown in Fig. 13.

5. Conclusions

The rapid Ag/Sn/Ag TLP bonding process assisted by the ultrasound was systematically investigated, and the following conclusions can be obtained:

- (1) The accelerated dissolution of Ag substrate and the extrusion of liquid Sn induced by complex sonochemical effects such as acoustic cavitation and streaming were responsible for the extremely rapid consumption of the “dynamic” transient liquid phase. High remelting point and robust joints fully consisted of Ag_3Sn IMCs were obtained at different temperatures within 15 s in air, in which the thickness of connection layer increased with the increase in bonding temperature, since the growth kinetics of the IMCs was as an exponent function of

temperature.

- (2) Under the effect of ultrasonic, an elongated scallop-like morphology of Ag_3Sn grains was developed at the Ag/Sn interface, accompanied by widening of grooves between neighbored grains. This phenomenon is called as a strengthening thermal grooving, and it can accelerate the dissolution of the substrate by promoting Ag atoms diffusion through the paths of stable molten channels. The acceleration of elemental diffusion was evaluated through the thickening kinetics of the Ag_3Sn IMCs, and it was conservatively estimated to be 6-16.5 times faster than the traditional TLP process.
- (3) The shear strength of the Ag_3Sn -based joint initially increased but lastly decreased with the increase in bonding temperature, with a highest value of 53.7 MPa. An excellent joint thermal reliability was experimentally verified by the high-temperature storage test at 350 °C. After aging for 120 h, the Ag/Sn/Ag bonded sample was principally composed of Ag(Sn) solid solution, and a number of (Ag, Ni) $_3\text{Sn}$ intermetallic particles orderly dispersed adjacent to both the Cu/Ag(Sn) interfaces. With storage time increasing from 120 to 240 h, similar microstructures were observed in the joints, and there were no heat cracks or any other defects within the connection layer.

Acknowledgement

This study is financially supported by the National Science Foundation of China under Grant No. 51375260, which is entitled “Technology and Mechanism of Low Temperature Transient Liquid Phase Bonding”.

References:

- [1]Neudeck PG, Okojie RS, Chen L, High-temperature electronics-a role for wide bandgap semiconductors? P. IEEE 90 (2002) 1065-1076.
- [2]Yoon SW, Glover MD, Shiozaki K, Nickel-tin transient liquid phase bonding toward high-temperature operational power electronics in electrified vehicles, IEEE T. Power Electr. 28 (2013) 2448-2456.
- [3]Lee J, Hwang H, Rhee M, Reliability investigation of Cu/In TLP bonding, J. Electron. Mater. 44 (2015) 435-441.
- [4]Ji H, Li M, Ma S, Li M, Ni $_3\text{Sn}_4$ -composed die bonded interface rapidly formed by ultrasonic-assisted soldering of Sn/Ni solder paste for high-temperature power device packaging, Mater. Design 108 (2016) 590-596.
- [5]Li JF, Agyakwa PA, Johnson CM, Kinetics of Ag_3Sn growth in Ag-Sn-Ag system during transient liquid phase soldering process, Acta Mater. 58 (2010) 3429-3443.
- [6]Li JF, Agyakwa PA, Johnson CM, Interfacial reaction in Cu/Sn/Cu system during the transient liquid phase soldering process, Acta Mater. 59 (2011) 1198-1211.
- [7]Shao H, Wu A, Bao Y, Zhao Y, Zou G, Interfacial reaction and mechanical properties for Cu/Sn/Ag system low temperature transient liquid phase bonding, J. Mater. Sci. Mater. Electron. 27 (2016) 4839-4848.
- [8]Liu B, Tian Y, Wang C, An R, Liu Y, Extremely fast formation of Cu-Sn intermetallic compounds in Cu/Sn/Cu system via a micro-resistance spot welding process, J. Alloy. Compd. 687 (2016)

667-673.

- [9]Sharif A, Gan CL, Chen Z, Transient liquid phase Ag-based solder technology for high-temperature packaging applications, *J. Alloy. Compd.* 587 (2014) 365-368.
- [10]Liu X, He S, Nishikawa H, Thermally stable Cu₃Sn/Cu composite joint for high-temperature power device, *Scripta Mater.* 110 (2016) 101-104.
- [11]Yang TL, Aoki T, Matsumoto K, Toriyama K, Horibe A, Mori H, Orii Y, Wu JY, Kao CR, Full intermetallic joints for chip stacking by using thermal gradient bonding, *Acta Mater.* 113 (2016) 90-97.
- [12]Xie R, Chen X, Lai Z, Liu L, Zou G, Yan J, Wang W, Microstructure, mechanical properties and mechanism of ultrasound-assisted rapid transient liquid phase bonding of magnesium alloy in air, *Mater. Design* 91 (2016) 19-27.
- [13]Ji H, Qiao Y, Li M, Rapid formation of intermetallic joints through ultrasonic-assisted die bonding with Sn-0.7Cu solder for high temperature packaging application, *Scripta Mater.* 110 (2016) 193.
- [14]Li M, Li Z, Xiao Y, Wang C, Rapid formation of Cu/Cu₃Sn/Cu joints using ultrasonic bonding process at ambient temperature, *Appl. Phys. Lett.* 102 (2013) 94104.
- [15]Chen X, Yan J, Gao F, Wei J, Xu Z, Fan G, Interaction behaviors at the interface between liquid Al-Si and solid Ti-6Al-4V in ultrasonic-assisted brazing in air, *Ultrason. Sonochem.* 20 (2013) 144-154.
- [16]Virot M, Chave T, Nikitenko SI, Shchukin DG, Zemb T, Mohwald H, Acoustic cavitation at the water-glass interface, *J. Phys. Chem. C* 114 (2010) 13083-13091.
- [17]Chinnam RK, Fauteux C, Neuenschwander J, Janczak-Rusch J, Evolution of the microstructure of Sn-Ag-Cu solder joints exposed to ultrasonic waves during solidification, *Acta Mater.* 59 (2011) 1474-1481.
- [18]Tan AT, Tan AW, Yusof F, Effect of ultrasonic vibration time on the Cu/Sn-Ag-Cu/Cu joint soldered by low-power-high-frequency ultrasonic-assisted reflow soldering, *Ultrason. Sonochem.* 34 (2017) 616-625.
- [19]Lis A, Leinenbach C, Effect of process and service conditions on TLP-bonded components with (Ag,Ni-)Sn interlayer combinations, *J. Electron. Mater.* 44 (2015) 4576-4588.
- [20]Chen H, Hu T, Li M, Zhao Z, Cu@Sn core-shell structure powder preform for high-temperature applications based on transient liquid phase bonding, *IEEE T. Power Electr.* 32 (2017) 441-451.
- [21]Deng X, Chawla N, Chawla KK, Koopman M, Deformation behavior of (Cu, Ag)-Sn intermetallics by nanoindentation, *Acta Mater.* 52 (2004) 4291-4303.
- [22]Bosco NS, Zok FW, Critical interlayer thickness for transient liquid phase bonding in the Cu-Sn system, *Acta Mater.* 52 (2004) 2965-2972.
- [23]Suslick KS, Didenko Y, Fang MM, Hyeon T, Kolbeck KJ, McNamara WB, Mdleleni MM, Wong M, Acoustic cavitation and its chemical consequences, *Philos. T. Roy. Soc. A* 357 (1999) 335-353.
- [24]Flint EB, Suslick KS, The temperature of cavitation, *Science* 253 (1991) 1397-1399.
- [25]Lis A, Park MS, Arroyave R, Leinenbach C, Early stage growth characteristics of Ag₃Sn intermetallic compounds during solid-solid and solid-liquid reactions in the Ag-Sn interlayer system: Experiments and simulations, *J. Alloy. Compd.* 617 (2014) 763-773.
- [26]Ghosh G, Interfacial microstructure and the kinetics of interfacial reaction in diffusion couples between Sn-Pb solder and Cu/Ni/Pd metallization, *Acta Mater.* 48 (2000) 3719-3738.
- [27]Kim YM, Roh H, Kim S, Kim Y, Kinetics of intermetallic compound formation at the interface between Sn-3.0Ag-0.5Cu solder and Cu-Zn alloy substrates, *J. Electron. Mater.* 39 (2010)

2504-2512.

- [28]Li J, Mannan S, Clode M, Chen K, Whalley D, Liu C, Hutt D, Comparison of interfacial reactions of Ni and Ni-P in extended contact with liquid Sn-Bi-based solders, *Acta Mater.* 55 (2007) 737-752.
- [29]Vassilev GP, Lilova KI, Gachon JC, Enthalpies of formation of Ni-Sn compounds, *Thermochim. Acta* 447 (2006) 106-108.
- [30]Flandorfer H, Saeed U, Luef C, Sabbar A, Ipser H, Interfaces in lead-free solder alloys: Enthalpy of formation of binary Ag-Sn, Cu-Sn and Ni-Sn intermetallic compounds, *Thermochim. Acta* 459 (2007) 34-9.
- [31]Frederikse HPR, Fields RJ, Feldman A, Thermal and electrical properties of copper-tin and nickel-tin intermetallics, *J. Appl. Phys.* 72 (1992) 2879.
- [32]Tian Y, Zhang QM, Li ZQ, Electrical transport properties of Ag₃Sn compound, *Solid State Commun.* 151 (2011) 1496-1499
- [33]Chromik RR, Vinci RP, Allen SL, Notis MR, Nanoindentation measurements on Cu-Sn and Ag-Sn intermetallics formed in Pb-free solder joints, *J. Mater. Res.* 18 (2003) 2251-2261.
- [34]Huang YL, Lin KL, Liu DS, Microstructure evolution and microimpact performance of Sn-Ag-Cu solder joints under thermal cycle test, *J. Mater. Res.* 25 (2010) 1312-1320.
- [35]Ocak Y, Aksöz S, Maraşlı N, Keşlioğlu K, Experimental determination of thermal conductivity and solid-liquid interfacial energy of solid Ag₃Sn intermetallic in the Sn-Ag-In ternary alloy, *Intermetallics* 18 (2010) 2250-2258.
- [36]Ghosh G, Elastic properties, hardness, and indentation fracture toughness of intermetallics relevant to electronic packaging, *J. Mater. Res.* 19 (2004) 1439-1454.
- [37]Ma D, Wang WD, Lahiri SK, Scallop formation and dissolution of Cu-Sn intermetallic compound during solder reflow, *J. Appl. Phys.* 91 (2002) 3312.
- [38]Kim HK, Tu KN, Totta PA, Ripening-assisted asymmetric spalling of Cu-Sn compound spheroids in solder joints on Si wafers, *Appl. Phys. Lett.* 68 (1996) 2204.
- [39]Kim HK, Tu KN, Kinetic analysis of the soldering reaction between eutectic SnPb alloy and Cu accompanied by ripening, *Phys. Rev. B* 53 (1996) 16027.
- [40]Lee J, Park J, Lee Y, Kim Y, Shin DH, Stability of channels at a scalloplike Cu₆Sn₅ layer in solder interconnections, *J. Mater. Res.* 16 (2001) 1227-1230.
- [41]Suslick KS, The chemical effects of ultrasound, *Sci. Am.* 260 (1989) 80-86.
- [42]Dybkov VI. Growth kinetics of chemical compound layers: Cambridge Int Science Publishing, 1998.
- [43]Cook GO, Sorensen CD, Overview of transient liquid phase and partial transient liquid phase bonding, *J. Mater. Sci.* 46 (2011) 5305-5323.