Microstructure characterization and mechanical behavior for Ag₃Sn joint produced by foil-based TLP bonding in air atmosphere

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Abstract: Low-temperature transient liquid phase (TLP) bonding for Ag-plated substrates was systematically investigated by using foil-based interlayer of pure Sn foil or preformed Sn/Cu/Sn sandwich structure in air atmosphere. The influences of bonding process, such as bonding temperature, bonding time and foil thickness, on the microstructure characterization and mechanical behavior of TLP joint were discussed. Experimental results show that Ag-plated substrates can be successfully TLP bonded in air atmosphere by the protection of flux. The formation of pores in intermetallic compounds (IMCs) is a serious problem for Ag/Sn/Ag TLP bonding, which is attributed to the volume shrinkage of isolated Sn areas during isothermal solidification. Prolonging homogenization time, properly increasing bonding pressure, decreasing temperature, or reducing interlayer thickness can effectively reduce the shrinkage porosity, but is still incapable of eliminating pores thoroughly. Both shear bands and intergranular facets are simultaneously observed on the fracture surface of Ag₃Sn joint. Since the micro voids distributing along Ag₃Sn grain boundaries weaken the cohesion strength between two neighboring Ag₃Sn grains in some areas. Using preformed Sn/Cu/Sn interlayer is available to enhance the mechanical integrity, which is strongly depended on the Cu thickness and Sn thickness. The joint shear strength can be increased by even more than 100% by the introduction of Cu foil. Moreover, the remained Cu layer in the IMCs can act as a buffer layer during fracture process, leading to the improvement of the ductility of TLP joint.

Keywords: TLP bonding; intermetallic compounds; pore; shear strength; fracture; ductility

1. Introduction

In recent years, the demand for high-temperature electronics, which require highly reliable and stable functionality, has been rapidly increasing in particular for the automotive, aerospace, deep-well drilling and energy production industries [1-3]. For example, deep oil and gas drilling will be performed in harsh environments in the near future, and the control and sensing devices inside need to survive pressure reaching to 30000 psi and temperature up to 300 °C for deeper exploration [3]. Thus, it will be an inevitable trend to substitute the conventional Si-based power devices for the wide band-gap (WBG) semiconductors such as SiC and GaN, since the former are limited to be operated less than 150°C while the latter are capable of electronic functionality above 300°C [2]. However, the unavailability of mature high-temperature packaging technology in the range of 300-600°C operation partially hinders development and application of WBG semiconductors. In the past, most candidates including Cu-Cu thermo-compression bonding [4], nano-silver particles sintering [5] and

low-temperature transient liquid phase (TLP) bonding [6] have been widely concerned by researchers in order to solve the technical problem of high thermal reliability for interconnections.

The low-temperature TLP bonding is a novel and promising die-attach technology for high-temperature applications. In this approach, a full intermetallic compounds (IMCs) joint is obtained at low temperature (generally < 300 °C) by the reaction between high-melting substrate (e.g. Cu, Ag) and low-melting interlayer (e.g. Sn, In). Thus, it can ensure devices withstand high temperature operations without failing [7]. Presently, many systems have been proposed, such as Cu-Sn [8], Ag-Sn [9], Au-Sn [10], Ni-Sn [11] and In-based systems [3, 7], and the mechanism of IMCs growth and thermal-mechanical reliabilities have been investigated. It is found that Ag₃Sn compounds have the best ductility in above systems [12], and both shear marks and dimples have ever been observed on the fracture surface of Ag₃Sn joint [13]. Furthermore, the pure Ag has superior physical property of ductility, high electrical and thermal conductivity, as well as excellent oxidation resistance [14]. Therefore, Ag-Sn system is a potential candidate in application to high-temperature packaging. Several coating approaches, such as electroplating, sputtering and vapor deposition [8], have been adopted to prepare film-based interlayer on the faying surface of substrate. At the same time, another familiar way is the employment of foil-based interlayer, which is sandwiched between two substrates, and will offer several advantages. On the one hand, this form of interlayer can be preformed independent of device and substrate, and reduces process cost compared with the deposition method. On the other hand, foil-based interlayer can easily adapt to the surface irregularities between two substrates due to its relatively larger thickness.

TLP bonding for Ag-Sn system has been rarely investigated by researchers, and is mainly focused on the growth mechanism and kinetics of Ag₃Sn IMCs. Lis et al. [15] studied the early-stage growth characteristics of Ag₃Sn grains via both experimental and numerical methods, and found that the morphology of Ag₃Sn grains was strongly depended on the temperature, while the predominant diffusion mechanism and coarsening effect were identified as temperature and time dependent at early stage. Li et al. [9] used pure Ag and Sn foils to determine the kinetics of scalloped Ag₃Sn growth, and confirmed the $t^{1/3}$ -dependence for Ag₃Sn thickening at temperatures of 260 °C, 300 °C and 340 °C, which was explained by the model of grain boundary/molten channel. Gollas et al. [16] employed thin Ag/Sn(1.5μm)/Ag electroplated layers for *in situ* X-Ray diffraction (XRD) measurements during annealing at 320 °C, and examined the transformation from Ag₃Sn into ζ-phase after 40 min and sequentially into Ag-Sn solid solution after 480 min. However, very few studies have been reported to the thermal-mechanical reliabilities of Ag-Sn TLP joint. Lis et al. [17] adopted Sn foil to join Ag-plated substrates under Ar shielding gas atmosphere, and obtained joints with maximum shear strength of 60 MPa, then further confirmed the excellent thermal stability for Ag-Sn system based on the microstructure annealed at 200 °C for 1200 h. Takahashi et al. [17] investigated high-temperature mechanical performances, and found that shear strength maintained an almost similar value of about 29 MPa from room temperature to high temperature (270 °C), and reached to more than 21.9 MPa until aging at 270 °C for 1200 h as well.

The Ag-Sn system TLP bonding has to be conducted under vacuum or inert gas atmosphere to prevent liquid phase from oxidation, while researches about thermal-mechanical properties are not enough to determine Ag-Sn IMCs reliability due to unstable process in different studies. In this work, microstructure characterizations and mechanical behaviors for TLP bonding of Ag-plated substrates were systematically investigated by using foil-based interlayer of pure Sn foil or preformed Sn/Cu/Sn sandwich structure. The objectives of this paper include: (i) realizing TLP bonding of Ag-plated

substrates with foil-based interlayer in air atmosphere; (ii) evaluating the effects of process such as bonding temperature, time and pressure on the microstructure and shear strength; (iii) understanding the mechanism of pores formation in Ag_3Sn layer; (iv) discussing the influences of Cu foil on the reduction of pores and mechanical properties of TLP joint.

2. Experimental procedures

Polished pure Cu (99.9%) rods with dimensions of 10 mm or 6 mm in diameter and 5.5 mm in length, were successively electroplated with 2 μm -thick Ni (P) layer and 45 μm -thick Ag layer as substrates. Before bonding process, the substrates were ultrasonically cleaned in 5vol. % HNO_3 solution for 5 min, followed by rinsing with deionized water and anhydrous alcohol, and dried at last. Commercially available pure Sn foil (99.9%) with 10 μm thickness was employed as interlayer, and firstly cleaned in acetone, then washed with anhydrous alcohol. Another form of interlayer, namely, preformed Sn/Cu/Sn composite structure, was also utilized to join Ag-plated substrates. In detail, it was fabricated by using pure Cu foil (10 μm , 20 μm or 50 μm) sandwiched between two Sn layers (plated film with 3 μm , or pure foil with 10 μm or 20 μm). The use of foil-based interlayer is beneficial to prevent solid-state diffusions between Ag and Sn, so that avoids the formation of defects described in [19]. Furthermore, the sandwich layer of Cu foil may improve ductility of TLP joint.

Fig. 1. (a) Schematic diagram of the assembly structure for bonding process; (b) temperature profile for specimen bonded at 300 °C for 90 min detected by a thermocouple

After cleaned, the faying surfaces of Ag-plated substrates were mildly coated on a small amount of rosin flux, then assembled with the foil-based interlayer, as depicted in Fig. 1a. TLP bonding process was conducted in a resistance furnace in air atmosphere. Bonding pressures ranging from 0.2 MPa to 1.0 MPa were applied by stainless steel blocks. A thermocouple was adopted to measure the real-time temperature profiles of sample, for instance, the temperature profile of 300 °C for 90 min was shown in Fig. 1b. The chosen bonding temperatures were 250 °C, 300 °C and 350 °C, respectively. The bonding time was determined by the thickness of Sn layer, within a range of 15 min to 300min.

The bonded samples were embedded in cold mounting resin, and successively ground with 240#, 600#, 1000#, 1500# and 2000# SiC sand papers, finally polished with diamond polishing solution. Cross-sectional analysis was carried out by using an optical microscope to investigate the microstructure. In order to evaluate joint mechanical reliability, shear test was performed on Gleeble-1500D thermal simulated test machine with a shear rate of 2 mm/min. Fracture surfaces of some typical joints were observed by a scanning electron microscope (SEM) equipped with energy disperse spectroscopy (EDS).

3. Results

3.1 Influences of bonding time on the microstructure and shear strength

TLP process for Ag/Sn/Ag sample was performed at 300 °C from 30 min to 300 min, and the evolution of microstructure and shear strength were investigated. For the joint bonded for 30 min (Fig. 2a), Ag₃Sn scallops on both sides impinged on each other, which led to the isolation of molten Sn into separated areas like islands. These Sn islands were mainly distributed in the middle of Ag₃Sn layer due to diffusion-driven reaction for TLP bonding. After full consumption of Sn (Fig. 2b), a large number of pores were formed along the central zone of the joint, and a thin layer of ζ -phase was found between Ag-plated substrate and Ag₃Sn layer. With prolonging bonding time (Figs. 2c and 2d), the ζ -phase layer could be notably observed, while the size and amount of defects slightly reduced. No noticeable variation in the thickness of ζ -phase could be observed though bonding time was prolonged from 90 min to 300 min, due to its slow growth rate in comparison to that of the Cu₃Sn [6]. In fact, the Ag/ ζ -phase interface (Fig. 2b) was much more planar than Ag/Ag₃Sn interface (Fig. 2a), which also indicated that the diffusivity of Ag atoms across ζ -phase was less than that in Ag₃Sn to some extent.

Fig. 2. Cross-sectional microstructure of Ag/Sn/Ag TLP joints bonded at 300 °C for: (a) 30 min, (b) 90 min, (c) 150 min, and (d) 300 min under the pressure of 0.3 MPa

Fig. 3. (a) Variation in joint shear strength with the bonding time for the process of 300 °C; and fracture surfaces of the TLP joints bonded for: (b) 30 min, (c) 90 min, and (d) 300 min

The variation in joint shear strength with the bonding time is shown in Fig. 3a. As can be seen, the measured value increases with increasing bonding time and reaches to the highest of approximately 30 MPa. We considered that the defects within the IMCs significantly affected the mechanical properties of joint, leading to a lower strength in comparison to the Cu/Sn TLP reaction [20]. From the fracture surfaces, it was found that oblique dimples were formed throughout the fracture surface of the joint containing Sn islands, due to the superior ductility of pure Sn (Fig. 3b); however, some Ag_3Sn grains were exposed by the ruptured Sn, accompanied by pores formation. Pronounced shear bands were observed on the fracture surface of Ag_3Sn joint, whereas the intergranular Ag_3Sn facets were also presented on the areas where there were many micro voids locating along Ag_3Sn grain boundaries (Fig. 3c). Additionally, with increasing bonding time to 300 min (Fig. 3d), the rupture path still propagated along the Ag_3Sn layer during shear test, but the shear marks occupied more areas of the fracture surface. It was suggested that this phenomenon might be associated with the reduction of micro pores during homogenization, and the failure mode was somewhat controlled by the pores along Ag_3Sn grain boundaries.

Although the pore defects probably are formed in the IMCs layer, the Ag/Sn/Ag sample can be successfully TLP bonded in air atmosphere via the use of flux. This method is helpful to simplify the TLP bonding process and reduces the process cost compared with the traditional process in vacuum or inert gas atmosphere. Therefore, studying the flux with good weldability for TLP bonding will be an important route to obtain excellent joint in air atmosphere.

3.2 Influences of bonding temperature on the microstructure and shear strength

Based on the joint composed of full Ag_3Sn IMCs, the bonding process on Ag/Sn/Ag sample was performed at 250 °C for 240 min and 350 °C for 60 min, respectively, in which parameters were determined by preliminary experiments. As shown in Figs. 4a and 4b, the two joints were consisted of similar microstructure but not for the mechanical integrity. Only few pores could be observed for the joint bonded at 250 °C, while the 350 °C bonded sample contained much more large-sized defects. This reveals that the pores in Ag/Sn/Ag TLP joint tend to be formed at higher temperature, in agreement with the study in [17].

Fig. 4. Cross-sectional microstructure of the Ag_3Sn joints bonded at: (a) 250 °C for 240 min and (b) 350 °C for 60

min under the pressure of 0.3 MPa; (c) Dependence of the Ag₃Sn joint shear strength on the bonding temperature; and (d) fracture surface for the joint bonded at 350 °C for 60 min

Fig. 4c shows the variation in shear strength of Ag₃Sn joint with the bonding temperature. It was found that the measured value slightly decreased with increasing bonding temperature, with the highest of more than 30 MPa, which was related to the change of pores in the joint. Fracture surface presented that both ductile and intergranular fracture features were observed for the joint bonded at 350 °C (Fig. 4d). Interestingly, it was carefully noted that many micro pores existed in the intergranular fracture areas, while the compact microstructure was observed in the shear-band zones. This also indicates that pores locating along the Ag₃Sn grain boundaries can significantly affect the fracture behavior of joint.

3.3 Influences of bonding pressure on the microstructure and shear strength

Based on the joint composed of full Ag₃Sn IMCs, TLP bonding for Ag/Sn/Ag sample was performed under different pressures varied among 0.2 MPa, 0.5MPa and 1.0MPa. Figs. 5 (a-c) show the microstructure. Large-sized pores were observed in the central zone of the IMCs layer when the bonding pressure was 0.2 MPa (Fig. 5a), and the porosity was distinctly reduced with the increase in bonding pressure at first (Fig. 5b). However, a great amount of flux was remained in the middle of the Ag₃Sn layer when relatively higher pressure was applied (Fig. 5c). The entrapped impurities of flux hindered the impingement and coalesce between Ag₃Sn scallops on both sides, and even induced the formation of pores in the joint. Thus, an appropriate high bonding pressure should be applied to reduce the pores and avoid the entrapped flux-impurities for the Ag/Sn/Ag TLP bonding in air atmosphere.

Fig. 5. Cross-sectional microstructure of the Ag₃Sn joints bonded at 300 °C for 90 min under pressure of: (a) 0.2 MPa, (b) 0.5 MPa, and (c) 1.0 MPa; (d) Variation in the Ag₃Sn joint shear strength with the bonding pressure; and (e) fracture surface for the joint bonded under the pressure of 1.0 MPa

Fig. 5d shows the variation in shear strength of Ag₃Sn joint with the bonding pressure. As can be seen, shear strength notably increases with the increase in bonding pressure initially, with the highest of 50.8 MPa under the pressure of 0.5 MPa, but then significantly reduced even lower than 10 MPa, due to the residual flux. Fig. 5e shows the fracture surface for the 1.0 MPa-pressure bonded sample. It could be found that many impurities of flux with aggregation state covered on the surfaces of Ag₃Sn scallops on the bottom substrate, which prevented Ag₃Sn grains on two different sides from contacting and coalescing with each other, accompanied by the formation of defects. The residual flux will greatly decline not only mechanical properties but also corrosion resistance of the TLP joint.

3.4 TLP bonding with preformed Sn/Cu/Sn interlayer

TLP bonding for Ag-plated substrates was performed at 300 °C for various time intervals by using Sn/Cu/Sn interlayer, which was composed of 10 μm-thick Cu foil and 10 μm-thick Sn foil. It is reported that no ternary alloy phases are formed in the Cu/Sn/Ag low-temperature TLP bonding, as detailed in [6]. Fig. 6 shows the cross-sectional microstructure. After 15 min (Fig. 6a), Ag₃Sn scallops on Ag-plated substrates contacted with Cu₆Sn₅ scallops on both sides of Cu layer, which made the residual Sn be isolated into many separated areas. Furthermore, very thin layers of Cu₃Sn could be observed on the cross section. After full consumption of Sn (Fig. 6b), Ag₃Sn layers impinged on the opposite Cu₆Sn₅ layers, and ζ-phase layers were emerged between Ag-plated substrates and Ag₃Sn layers, while Cu₃Sn layers significantly thickened due to solid-state diffusions of Cu atoms. The Cu₆Sn₅ IMCs were totally disappeared when the bonding time was prolonged to 150 min (Fig. 6c). With continuing reaction (Fig. 6d), the microstructure was not greatly changed by the homogenization, while the pores were noticeably reduced in comparison to the Ag/Sn/Ag bonded sample. Moreover, the embedded Cu layer was always decreased but could not be vanished under this bonding process. It was interesting to note that the thicknesses of full IMCs (about 20 μm) between Ag-plated substrate and Cu layer were generally less than that of the Ag/Sn/Ag TLP joints (about 32 μm), which was caused by the squeezing out of molten Sn. We supposed that this process might lead to the reduction of pores.

Fig. 6. Cross-sectional microstructure of Ag/Sn/Cu/Sn/Ag samples bonded at 300 °C for:
(a) 15 min, (b) 90 min, (c) 150 min and (d) 300 min under the pressure of 0.3 MPa

Fig. 7a shows the variation in joint shear strength with the bonding time. It was found that the measured value increased with bonding time, with the highest of exceeding 35 MPa, especially for some samples even more than 40 MPa, which was generally higher than that of the Ag/Sn/Ag bonded samples. This difference was related to the reduction of pores in the IMCs layer. We suggested that the insertion of Cu foil between Sn foils changed the joint microstructure, in particular the growth process of IMCs grains, so that reduced the pores. However, the detailed mechanism should be further investigated.

Fig. 7b shows the fracture surface of the joint bonded at 300 °C for 90 min. It could be found that many dispersive “islands” of Cu/Cu-Sn IMCs, determined by the EDS analyses, located in the crowd of Ag₃Sn IMCs. And remarkable boundaries existed between the Cu and Ag elemental distributions, in agreement with the SEM image of the fracture. Thus, it can be deduced that the failure path mainly propagates along the interface between Ag₃Sn and Cu-Sn IMCs, and also passes through the residual

Cu layer. A typical area of the ruptured Cu was magnified under SEM, as shown in Fig. 7c, it was found that many noticeable shear bands were produced throughout the ruptured Cu layer. This indicated that the embedded Cu foil might act as a buffer layer during shear test and improved the ductility of TLP joint.

Fig. 7. (a) Dependence of shear strength of joint obtained at 300 °C on the bonding time; (b) fracture surface of the joint bonded at 300 °C for 90 min; (c) shear bands on the remained Cu fracture at the edge of Cu/Cu-Sn IMCs; and the others are the elemental mapping images of Cu, Sn, Ag atoms in (b)

In fact, the improvement of ductility can be also verified by the shear process curve, as shown in Fig. 8. The shear force increases with the stroke (time) initially until reaches to a highest value, which means the actual shear force that makes the bonded sample rupture, then gradually declines to the lowest. The declined curving segment represents the fracture process of the joint, and its declining rate (slope) can be used to evaluate the ductility somewhat. Interestingly, the fracture process curve nearly vertically lowers down for the Sn foil bonded sample, while that of the Sn/Cu/Sn bonded sample slowly declines to the original value. The difference of curve slope indicates that the ductility of TLP joint is improved by the insertion of Cu foil.

Fig. 8. Variations in Shear force with stroke (time) for TLP joints bonded with (a) pure Sn foil and (b) preformed Sn/Cu/Sn interlayer

In order to further understand the improvement of mechanical properties by the addition of Cu foil, the influences of Cu foil thickness and Sn foil thickness on the microstructure and shear strength were investigated. Two schemes were adopted to fabricate Sn/Cu/Sn sandwich interlayer. The one is changing the thickness of Cu foil among 10 μm , 20 μm and 50 μm based on the 10 μm -thick Sn foil,

and the other is changing the thickness of Sn layer among 3 μm (obtained by electroplating), 10 μm and 20 μm based on the 10 μm -thick Cu foil. TLP bonding process was performed under different conditions, with the joints composed of full intermetallic phases. In detail, the Cu-thickness-changed samples were bonded at 300 $^{\circ}\text{C}$ for 90 min, while the Sn-thickness-changed samples were bonded at 300 $^{\circ}\text{C}$ for 45 min for 3 μm -thick Sn layer and 180 min for 20 μm -thick Sn foil, respectively. Following, the cross-sectional analysis was carried out to investigate the microstructure, as shown in Fig. 9.

Fig. 9. Cross-sectional microstructure of Ag/Sn/Cu/Sn/Ag samples bonded at 300 $^{\circ}\text{C}$ for 90 min with Cu thickness of (a) 20 μm and (b) 50 μm ; and 300 $^{\circ}\text{C}$ for (c) 45 min with 3 μm Sn layer and (d) 180 min with 20 μm Sn layer. In addition, the bonding pressure was applied with 0.3 MPa

For the 20 μm Cu foil bonded sample (Fig. 9a), the microstructure was similar to that of the 10 μm Cu foil bonded sample, whereas fewer pores could be observed and lesser Cu_6Sn_5 IMCs remained in the joint. In addition, the thickness of full IMCs layer (about 16 μm) between Ag-plated substrate and Cu layer was less than that of the 10 μm Cu foil bonded sample. With the increased Cu foil thickness to 50 μm (Fig. 9b), approximately no pores could be found on the cross section, and the Cu_6Sn_5 compounds were completely consumed, while the thickness of IMCs layer between Ag-plated substrate and Cu foil was reduced compared with the thinner Cu layer bonded samples, merely about 13 μm . It was suggested that the change of IMCs thickness between Ag-plated substrate and Cu layer was attributed to the squeezing out of molten Sn, which also affected the formation of pores in the TLP joint. For the joint bonded with 3 μm Sn (Fig. 9c), there were many pores concentrated at the boundaries of the Cu_3Sn phases, and almost no Ag_3Sn formed in these areas. This type of pore was same as the study in [19]. In detail, there was no more molten Sn to react with the Ag-plated substrate during isothermal solidification due to Cu/Sn reactions at solid state, which induced pores formation at the Ag/ Cu_3Sn interface, as highlighted in the white marks. For the 20 μm Sn bonded sample (Fig. 9d), the microstructure was very similar to that of the 10 μm Cu foil, but almost no pores could be observed and very thin Cu layer remained on the cross section.

Fig. 10 Influences of Cu thickness and Sn thickness on the shear strength of TLP joint. Wherein, the joints are fully composed of IMCs with microstructure shown in Figs. 6 and 9.

Fig. 10 shows the variations in joint shear strength with the Cu foil thickness and Sn layer thickness. It can be found that shear strength increases with increasing both Cu thickness and Sn thickness, and the highest value even exceeds more than 70 MPa, far more than the Sn foil bonded samples. It was suggested that the pores and residual Cu thickness played an important role to determine the mechanical properties of TLP joint, and the insertion of Cu foil could effectively reduce the defects.

Fig. 11 Fracture surfaces of TLP joint bonded by using the preformed Sn/Cu/Sn interlayer of: (a-b) 50 μm Cu foil, (c-d) 3 μm Sn layer, and (e-f) 20 μm Sn foil

Fracture analysis was carried out to investigate the influence of remained Cu layer on the joint rupture behaviors, as shown in Fig. 11. For the 50 μm Cu foil bonded sample, many irregular Cu/Cu-Sn IMCs “islands”, identified by the EDS analyses, distributed among the ruptured Ag_3Sn IMCs (Fig. 11a). Moreover, a typically dark-colored island area highlighted by the arrow was magnified in the SEM, and we found that shear bands of ruptured Cu horizontally extended throughout the fracture surface (Fig. 11b). This indicated that failure path propagated not only along the IMCs but also within the remained Cu layer, and the cohesion strength between Ag_3Sn and Cu-Sn IMCs was enhanced by the reduction of pores. Thus, it could be concluded that the soft Cu microstructure acted as a buffer layer during rupture process and improved strength and ductility of the joint. For the 3 μm Sn bonded sample, a bulk Cu/Cu-Sn IMCs nearly occupied the entire fracture surface, and some warped areas (in the hidden-line mark) were formed after shear test (Fig. 11c). The Cu/Cu-Sn IMCs area was clearly exhibited in Fig. 11d, both Cu_3Sn grain facets and Cu_6Sn_5 scallops were presented with their original morphologies, but not fracture topographies. Hence, we considered that the cohesion strength between Ag_3Sn and Cu-Sn

IMCs under this condition was very terrible, due to continuous pores as mentioned above. For the 20 μm Sn bonded sample, Cu/Cu-Sn IMCs islands uniformly located on the fracture surface (Fig. 11e), due to relatively thin Cu layer and compact IMCs microstructure. The ruptured Cu surface was presented with a tearing feature (Fig. 11f), and created a bevel angle with the Ag_3Sn ruptured surface.

4. Discussion

4.1 Mechanism of pore formation

Some other factors should be considered to discuss the mechanism of pore formation except for the impact of entrapped flux. In order to clearly observe the appearance of pore, 25 μm Sn foil was used to join Ag-plated substrates under vacuum condition, and the microstructure was shown in Fig. 12. It was found that some large-sized pores started to form in the Sn islands when Ag_3Sn scallops on both sides contacted with each other (Fig. 12a), and their sizes significantly increased after the Sn islands were completely consumed (Fig. 12b), which were remarkably larger than those of joints bonded with 10 μm Sn foil (Fig. 5a). We suggested that the formation of pores was attributed to the volume shrinkage of Sn-islands during isothermal solidification, according to the change of the pore size. Such pores were quite different from the defects in [19, 21], which formed prior to the occurrence of liquid phase. Since no enough liquid was available to successfully accomplish TLP bonding at targeted temperature, due to solid-state reactions during heating stage.

Fig. 12. Characterization of the pores in Ag-Sn TLP joints bonded at 280 °C for: (a) 150 min (remaining Sn islands), and (b) 300 min (fully composed of IMCs); wherein, the bonding pressure is about 0.2 MPa

It was calculated that the process of Ag-Sn reaction and conversion into Ag_3Sn IMCs led to volume contraction of approximately 9% in theory [17], which also demonstrated the shrinkage pore in this study. However, what are the factors that determine the shrinkage porosity? According to the mass conservation, the size of shrinkage pore can be expressed as follow

$$\Delta V = \frac{3(1-\eta)m_{\text{Sn}}}{\eta\rho_{\text{Ag}}} + \frac{m_{\text{Sn}}}{\rho_{\text{Sn}}} - \frac{m_{\text{Sn}}}{\eta\rho_{\text{Ag}_3\text{Sn}}} = \alpha m_{\text{Sn}} \quad (2)$$

where m_{Sn} is the mass of the Sn island; ρ_{Sn} , ρ_{Ag} and $\rho_{\text{Ag}_3\text{Sn}}$ are the densities of Sn, Ag and Ag_3Sn , respectively; η is the molar mass fraction of Sn in Ag_3Sn ; and α is the coefficient of shrinkage pore, which is calculated as 0.537. From Eq. 2, the probability of shrinkage pore could be evaluated by the amount of Sn islands. In fact, the Ag_3Sn grains in different areas have different growth rates because of anisotropic mass flow [17], so the wave-shaped Sn/ Ag_3Sn interface is produced, which will significantly affect the Sn islands. According to the above experiments, the shrinkage pores in Ag/Sn/Ag TLP joint increased with increasing temperature, decreasing bonding pressure, or thickening Sn foil.

Lis et al. [15] used the interfacial roughness of Sn/ Ag_3Sn interface to describe the scalloped shape of Ag_3Sn grains, as well as the amount of Sn islands. They found that the value was strongly depended

on the bonding temperature, and increased in the process of higher temperature. In addition, the previous study indicated that some other shapes of Ag_3Sn grains, such as column and abnormal large-sized plate, were more easily generated at higher temperature [22], which led to much more Sn islands during isothermal solidification. The two phenomena indicate that the bonding temperature can affect the amount of Sn islands via two ways, the difference of Ag_3Sn scallops in height and the morphologies of Ag_3Sn grains.

The thickness of Sn foil determined the reaction time when Ag_3Sn scallops on both substrates contacted with each other, and further affected the amount of the Sn islands. This can be explained by the following equation [22]:

$$t = \frac{\pi W_o^2}{16 D_s C_{\max}^2} \quad (3)$$

where t is the reaction time; W_o is the width of interlayer; D_s is the diffusivity of Ag atoms in molten Sn; and $C_{\max}$ is the maximum concentration of dissolved Ag atoms. From this equation, the reaction time increased with the increase in interlayer thickness. However, the difference of IMCs scallops in height was somewhat determined by the reaction time, as detailed elsewhere [24]. Thus, it could be considered that the amount of Sn islands was associated with the thickness of interlayer through the change of Sn/ Ag_3Sn interfacial roughness. It must be pointed out that so-called reaction time in this part was different from the bonding time. In fact, this model could also be used to explain the reduction of pores when using preformed Sn/Cu/Sn interlayer, as part of the molten Sn was squeezed out.

In summary, a lower bonding temperature, higher bonding pressure or thinner interlayer is useful to reduce the pores in Ag/Sn/Ag TLP bonding, but still incapable of eliminating them thoroughly. However, the chosen interlayer should not be less than the critical thickness described in [19], or other kinds of pores will be produced. And the bonding pressure was not too high in consideration of the residual flux in IMCs and the damage for fragile devices.

4.2 Fracture behaviors of Ag_3Sn joint

For the Ag/Sn/Ag TLP bonding, both shear bands and intergranular facets were simultaneously observed on the fracture surface of Ag_3Sn joint. This is incompletely same with the report that shear marks extend over all the fracture surface in other work [17]. It was found that the pores distributing along Ag_3Sn grain boundaries noticeably affected the fracture mode from the above analyses. Fig. 13 shows the fracture surfaces of two different typical Ag_3Sn joints, which contained many voids or not. In the pore-containing joint (Fig. 13a), many rock-candy shaped Ag_3Sn grain facets, implying brittle fracture mode, occupied across the fracture surface, while very few shear bands were observed. However, shear bands almost extended throughout the fracture surface of the joint containing few pores (Fig. 13b), accompanied by few intergranular facets where pores existed.

Fig. 13. Fracture surfaces of the joint containing: (a) many micro voids and (b) very few pores; and (c) model of crack propagation in the Ag_3Sn joint

Crack propagation is dominated by the maximal stress principle and minimal energy (or strength) principle in the failure [25]. Wherein, the minimal strength principle points out that the direction of crack growth follows the path with a minimal expanding resistance. In addition, the relationship between grain boundary strength and intragranular strength determines the direction of crack propagation, either into or along grains. Thus, the grain boundary is very important for the rupture behaviors of polycrystalline metal. Grain boundary character distribution (GBCD), which describes the type and frequency of grain boundaries, is proven to be an important microstructural factor affecting fracture processes and characteristics [26]. Impurity segregation to grain boundaries generally weakens cohesion of grain boundary, and induces grain boundary embrittlement [27, 28].

We considered that the pores locating along grain boundaries should be carefully concerned to discuss the fracture behaviors of Ag_3Sn joint. Fig. 13c shows the specific model of crack propagation in the IMCs during shear test. In general, the fracture was prone to proceed through the Ag_3Sn grains according to the above results, then the shear bands were generated parallel on the force direction. However, the existence of micro voids weakened the cohesive strength of Ag_3Sn grain boundaries, which brought that the cracks also initiated in the pores and propagated along grain boundaries. Furthermore, the pores were randomly distributed in different areas of joint due to the inhomogeneity of microstructure, leading to the formation of both shear bands and intergranular facets in the fracture.

4.3 Improvement of mechanical properties by the addition of Cu foil

According to the above experiments on preformed Sn/Cu/Sn interlayer TLP bonding, the fracture models were established for different typical joints, in which three kinds of fracture modes were distinguished based on the thickness of residual Cu layer in the IMCs. In detail, if the Cu layer is very thin (Fig. 14a, mode I), such as 20 μm Sn foil bonded sample, the cracks will uniformly pass along the IMCs and through the Cu layer; however, if the Cu layer is relatively thicker (Fig. 14b, mode II), such as 3 μm and 10 μm Sn bonded samples, the cracks will randomly propagate along the IMCs and through the Cu layer; and if the Cu layer is much thicker (Fig. 14c, mode III), such as 20 μm and 50 μm Cu bonded samples, the cracks will randomly extend along the IMCs and through even within the residual Cu layer. The process belonging to fracture mode I or mode III can more significantly improve the mechanical properties than that of the mode II.

Fig. 14. Fracture models for different typical TLP joints bonded by preformed Sn/Cu/Sn interlayer: (a) mode I-cracks uniformly propagate through thin residual Cu layer, such as 20 μm Sn bonded sample; (b) mode II-cracks randomly propagate through thicker residual Cu layer, such as 3 μm and 10 μm Sn bonded samples; (c) mode III-cracks randomly propagate through even within much thicker residual Cu layer, such as 20 μm and 50 μm Cu bonded samples.

The increase of joint shear strength was realized by the introduction of Cu foil between IMCs layers, in particular for the thick Cu or Sn foil bonding situation (about 100%). This was attributed to the reduction of pores and enhancement of cohesion strength between Ag_3Sn and Cu-Sn IMCs. In addition, the ductility was also improved by the remained Cu layer, from no matter whether the shear process curve or shear bands on the fracture surfaces. As naturally brittle materials, the IMCs can lead

to embrittlement of TLP joint, but how does the Cu layer improve the ductility?

Since the cohesion strength between dissimilar IMCs (e.g. $\text{Cu}_6\text{Sn}_5/\text{Ag}_3\text{Sn}$) was increased by the improvement of mechanical integrity, cracks could propagate through the ductile Cu layer with three modes depicted in Fig.14. It was suggested that the embedded Cu layer acted as a buffer layer and absorbed much fracture energy in the rupture process of joint, which was similar to the mechanism of ductile phase strengthening [29], while the Cu layer was just a continuously banded structure but not with a form of micro particles. As shown in Fig. 14, we consider that if more cracks can vertically or horizontally propagate through the remained Cu layer, the improvement of ductility will be more significant. In fact, this can be achieved by the optimization of Cu/Sn ratio, based on the change of residual Cu thickness in the IMCs.

5. Conclusions

In the present study, TLP bonding for Ag-plated substrates using Sn foil or preformed Sn/Cu/Sn interlayer was realized in air atmosphere by the protection of flux. Based on the preceding experimental results and analyses, the following conclusions can be drawn:

1) There exists a serious problem in Ag/Sn/Ag TLP bonding, which is the formation of pores in the middle of Ag_3Sn layer. Such defects are caused by volume shrinkage for Sn islands conversion into IMCs during isothermal solidification. Prolonging homogenization time, adopting lower bonding temperature, properly reducing interlayer thickness or applying higher bonding pressure can usefully reduce the shrinkage pores, but still incapable of eliminating them thoroughly. However, the bonding pressure should not be too high in consideration of the entrapped impurities of flux in the IMCs.

2) Shear strength of Ag/Sn/Ag TLP joint is strongly depended on the bonding time, temperature, and pressure, due to the change of mechanical integrity. The highest shear strength for Ag_3Sn joint is evaluated to be 50.3 MPa under the bonding pressure of 0.5 MPa. Both shear bands and intergranular facets are simultaneously observed on the fracture surface of Ag_3Sn joint. It is because that the micro voids, distributing along Ag_3Sn grain boundaries, weaken the cohesion strength between two neighboring Ag_3Sn grains in some areas.

3) Using preformed Sn/Cu/Sn interlayer is able to significantly improve the mechanical integrity, in particular for the thick Cu or Sn foil bonding situation. The shear strength has been improved even more than 100% by the remained Cu layer in the TLP joint. Both Cu thickness and Sn thickness are important to decrease the formation of pores, and affect the mechanical properties. The fracture path extends not only along the IMCs but also through the Cu layer. Moreover, the residual Cu layer between two different IMCs layers can act as a buffer layer during failure process and improve the ductility of joint, with a mechanism like ductile phase strengthening.

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