

Transient liquid phase bonding in the Cu-Sn system

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Abstract

Purpose – This paper aims to study the features of microstructures and mechanical properties of the joints which were produced by transient liquid phase method. The difference between phases in bonding region identified through metallography pictures and applying hardness and shear strength tests.

Design/methodology/approach – The bonding process was carried out at a temperature of 300°C for time durations ranging from 15 to 120 min. The scanning electron microscopy equipped with energy dispersive spectroscopy system and optical microscopy were used to examine microstructural characteristics, and mechanical properties of the joints were studied by applying microhardness and shear tests. The shear tests were conducted by a shear fixture which was mounted on the tensile machine.

Findings – The intermetallic compounds of the Cu_6Sn_5 – η and the Cu_3Sn – ε were formed simultaneously in the bonding interface. Although the η -phase, which exhibits scallop-shaped morphology, grows very quickly, upon completion of the isothermal solidification stage, it turns into the ε -phase. The hardness of the bonding interface is significantly higher than that of the substrate. The shear results show that once the bonding process is complete, brittle fracture occurs. Moreover, a greater decrease in strength was observed when the ε -phase is the only phase in the bonding region.

Originality/value – The hardness number of the η -phase is higher than that of the ε -phase. The hardness numbers of the η -phase and the ε -phase are 894 and 689 HV, respectively. The mean shear strength values of the samples that were bonded at 300 °C for 15, 60 and 120 min were 11.7, 9.5 and 5.4 MPa, respectively.

Keywords Intermetallic compounds, Shear strength, Microhardness, Isothermal solidification, Microelectronics, Transient liquid phase

Paper type Research paper

Introduction

Due to their low thermal stability, conventional solders cannot be used in manufacturing for high-temperature applications, such as chip stacking, multi-chip assembly or 3D integration (Lee and Wang, 1993; Eagar and Hoh, 1992; Bernstein, 1966; Bartels *et al.*, 1994; Tollefsen *et al.*, 2012; Rodriguez *et al.*, 2013; Lee *et al.*, 2015; Huebner *et al.*, 2006; Klumpp *et al.*, 2004; Lapadatu *et al.*, 2010; Jung *et al.*, 2018; Natzke and Grossner, 2017). Likewise, the use of high-temperature bonding technologies may result in irreparable damage to devices, as it causes a mismatch of the coefficient of thermal expansion among the different layers, and this triggers high thermodynamic stress (Tollefsen *et al.*, 2012; Rodriguez *et al.*, 2013; Lee *et al.*, 2015).

Given these limitations, it is vital to use a bonding technique that offers a low processing temperature, while at the same time resulting in a higher remelting temperature.

Transient liquid phase (TLP) bonding (also known as solid-liquid interdiffusion) is promising in terms of fulfilling these requirements, and due to its ability to produce at low temperatures joints which remain solid and strong well above

the bonding temperature is one of several viable bonding technologies that has recently been attracting a lot of attention in the microelectronics field (William *et al.*, 1998; Bosco and Zok, 1998; Li *et al.*, 2011; van de Wiel *et al.*, 2012; Chu *et al.*, 2015; Liu *et al.*, 2012).

In the TLP process, a very small amount of Pb-free solder is used, all of which are converted into high temperature intermetallic phases under isothermal solidification. The mechanical properties of these thin joints (which typically measure less than 5 μm in thickness) are superior to those of a conventional solder (Bartels *et al.*, 1994; Zhao *et al.*, 2013; Lee *et al.*, 2010).

There are a number of Pb-free alloy systems (such as Au-Sn, Au-In, Cu-In and Cu-Sn) that are currently being used for TLP bonding. Gold-based systems are costly, while indium is susceptible to oxidation. Copper-based systems, on the other hand, have good thermal and electrical properties and are considerably less expensive and more accessible. In addition, the low melting point of tin and its solubility with copper render

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the copper-tin system more suitable than other systems for further investigation (William *et al.*, 1998; Bosco and Zok, 1998; Li *et al.*, 2011; van de Wiel *et al.*, 2012).

In this paper, TLP bonding was used to investigate microstructure features and mechanical properties of the joints of the copper-copper bonds using a tin interlayer at a temperature of 300°C and for time durations ranging from 15 to 120 min.

Materials and experimental method

In this research, copper with dimensions of $10 \times 10 \times 4 \text{ mm}^3$ was used as the base metal, and tin with a thickness of $25 \mu\text{m}$ was used as the interlayer. The nominal compositions of the base metal and the interlayer are shown in Tables I and II, respectively.

Prior to bonding, the contact surfaces of the base metals were ground and slightly polished. The interlayer was then sandwiched between two pieces of polished Cu substrates. In order to ensure that both parts of the assembly remained in close contact with each other during the bonding process, the samples were inserted into a holding fixture (Figure 1).

The TLP process was conducted under argon gas in a horizontal tube furnace at 300°C for durations of 15, 60 and 120 min. In terms of Metallography, the cross sections were ground and polished using a $0.06 \mu\text{m}$ alumina-based medium. Microstructural examinations were conducted under optical microscopy and scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS) system. Microhardness tests were performed using a Buhler microhardness tester under an indentation load of 25 g for 10 s.

The shear test was conducted in a universal machine (Z250-Zwick) using a shear fixture, which is shown in the schematic diagram in Figure 2. Three shear samples for each group of process parameters were tested under a maximum load of 2 kN with a displacement rate of 0.5 mm min^{-1} . The fracture surface of the shear samples was analyzed using SEM and an EDS system.

Results and discussion

Microstructure

Figure 3 depicts an SEM micrograph of the bonded sample for 15 min at 300°C. As can be seen, there are three distinct phases in the bonding region: the scallop-shaped phase, a very thin undulated gray layer and a dark, bright phase in the center of bonding.

EDS analysis shows that the chemical composition of the scalloped phase is 53.76 at. % Cu and 46.24 at. % Sn, which is

very close to that of the intermetallic compound $\text{Cu}_6\text{Sn}_5 - \eta$. Meanwhile, the composition of the bonding center is close to that of the Sn interlayer, while the result for the undulated layer was not obtainable, due to it being too small ($< 2 \mu\text{m}$) to be measured by the EDS system. However, based on previous research, this phase is related to the intermetallic compound $\text{Cu}_3\text{Sn} - \varepsilon$.

Figure 1 3D image of holding fixture

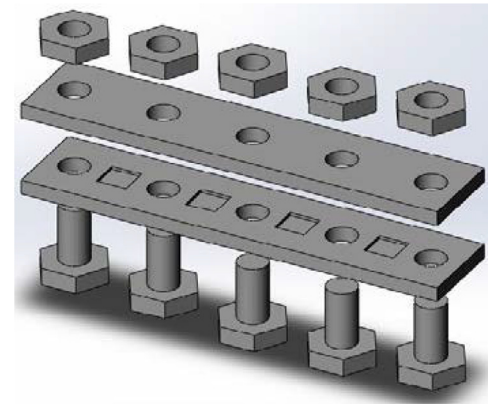


Figure 2 Schematic diagram of the shear fixture

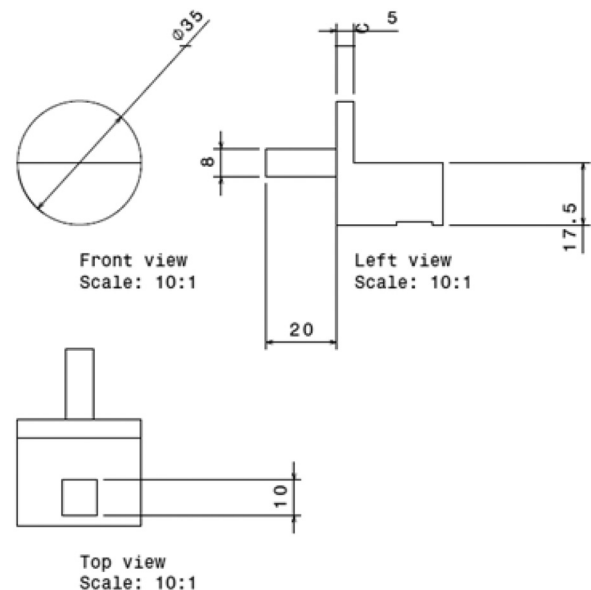


Table I Chemical composition of the base metal

Element	Zn	Pb	Sn	P	Mn	Fe	Al	Bi	Sb	Cr	Cu
Wt. %	0.978	0.009	0.019	0.009	0.008	0.043	0.009	0.005	0.008	0.004	bal

Table II Chemical composition of the interlayer

Element	As	Ca	Cu	Fe	K	Mg	Na	Ni	Al	Sn
Wt. %	0.011	0.0017	0.022	0.0046	0.0013	0.0017	0.0061	0.0022	0.0015	bal

Figure 3 SEM image of sample bonding at 300°C for 15 min

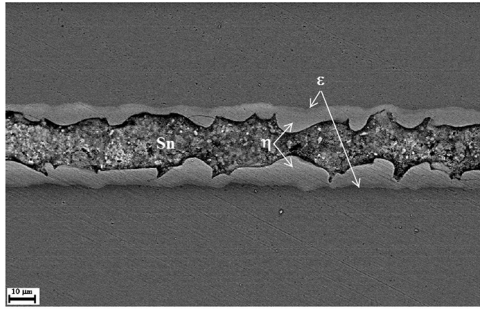


Figure 4 shows the sample bonded at a temperature of 300°C for 60 min. As can be seen, the bonding region contains two phases: a gray phase on both sides of the bonding interface, and a bright phase in the middle of the bonding interface. In addition, the whole Sn interlayer has consumed. The EDS analysis of this sample indicated that the chemical composition of the phase in the middle of the bonding was 44.2 at. % Sn and 55.8 at. % Cu, which is very similar to that of the η -phase.

In the case of the phase in between the Cu_6Sn_5 and the Cu, the weight percent is equal to 74.26 at. % Cu and 25.74 at. % Sn, which is nearly equivalent to that of the ε -phase.

With respect to the TLP process that was carried out for 120 min at 300°C, the η -phase has completely disappeared, and, as can be seen in **Figure 5**, the bonding interface is now only contained the ε -phase.

Figure 4 SEM image of sample bonding at 300°C for 60 min

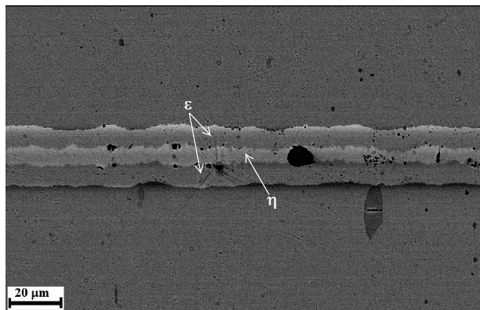
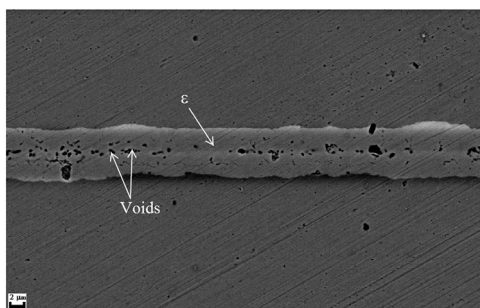


Figure 5 SEM image of sample bonding at 300°C for 120 min



The result of the EDS analysis also indicated the presence of the ε -phase. There are obvious voids in the center of the ε -phase. The formation of such voids is inevitable in solid-state diffusion couples of copper-tin, causing some problems in terms of the integrity of the bonding.

Mechanical properties

Microhardness

Figure 6 shows the microhardness profiles of the bonded samples which were measured across the bonding center at the temperature of 300°C during bonding from 15 to 120 min. It is evident that the bonding interface, which contains intermetallic compounds, has a significantly higher hardness than the surrounding area. In addition, the hardness of the η -phase is greater than that of the ε -phase. The Vickers hardness numbers of the η -phase and the ε -phase are 894 and 689 HV, respectively.

Figure 7 shows the optical micrograph of indentation marks on the sample which was bonded at 300°C for 30 min. Clearly, the marks on the Cu substrates are greater than those on the interface, which denotes a noticeable difference between the hardness of the bonding interface and that of the copper substrate.

Figure 6 effect of holding time on microhardness across bonding line at 300°C

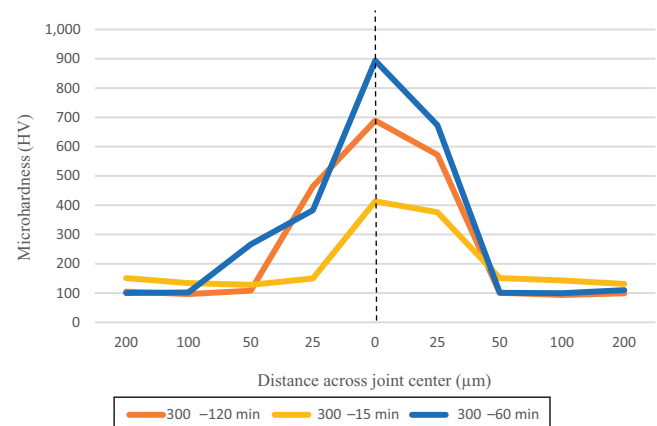
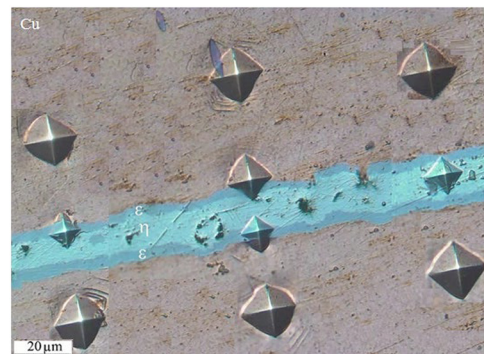


Figure 7 Optical micrograph of indentation marks on bonding sample after 30 min at 300°C



Furthermore, the marks on the interface between the η layer and the ε layer are smaller than those on the η -phase, which indicates that the interfacial layer between the η -phase and the ε -phase is more resistant to deformation than the η -phase.

Shear test

Figure 8 illustrates the load-displacement curves for each group of process parameters. The graphs show the relationship between the fracture load and the duration of the bonding process.

When the TLP process was completed and the joints were completely transformed into intermetallic compounds, a reduction in the failure load was observed. The mean shear strength values of the samples that were bonded at 300°C for 15, 60 and 120 min were 11.7, 9.5 and 5.4 MPa, respectively. These values were calculated by dividing the maximum load by the cross sectional area.

Figure 8(a) shows the mechanical behavior of the samples bonded for 15 min at 300°C. In this condition, the bonding process is not fully developed; as evidenced by the SEM micrograph shown in Figure 3, there is some Sn interlayer in the bonding interface. The occurrence of plastic deformation is due to the Sn interlayer in the center of bonding. Figures 8(b) and (c) depict the samples that were bonded at 300°C for 60 and 120 min, respectively. The Sn has completely disappeared, and the entirety of the bonding region is now converted into intermetallic compounds. As can be seen, the load has increased linearly and without displaying any plastic deformation, the brittle fracture has taken place in the elastic region. The lower fracture load for the single ε -phase samples is due not only to the presence of the intermetallic compound but also to the presence of voids that developed in their bonding

center. Previous studies (Nai *et al.*, 2009; Choudhury and Ladani, 2016; Deng and Chawla, 2004; Dirnfeld and Ramon, 1990) also showed that as the thickness of the intermetallic compounds increased, the shear strength of the bonded samples decreased.

Fractography

Figure 9 shows the fracture surface of the two-phase interface of the bonded sample for 60 min, which contains intermetallic compounds. As can be seen, on the fracture surface there are sugar-like grains and a smooth, circle-shaped phase. The EDS results indicated that a smooth surface is associated with the presence of the η -phase, and the sugar-like grains indicate the presence of the ε -phase. This type of morphology shows that fracture has taken place in the interfacial η/ε layer. It also confirms the microhardness results, which indicated that the interface between η/ε exhibits strong resistance to deformation.

Figure 9 Fracture surface of the two-phase sample of η and ε

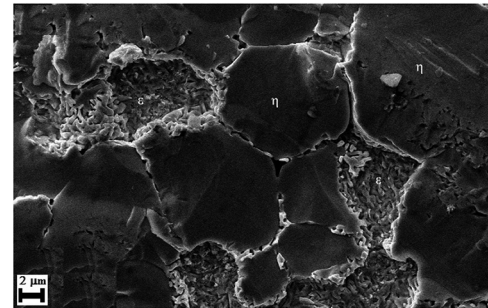
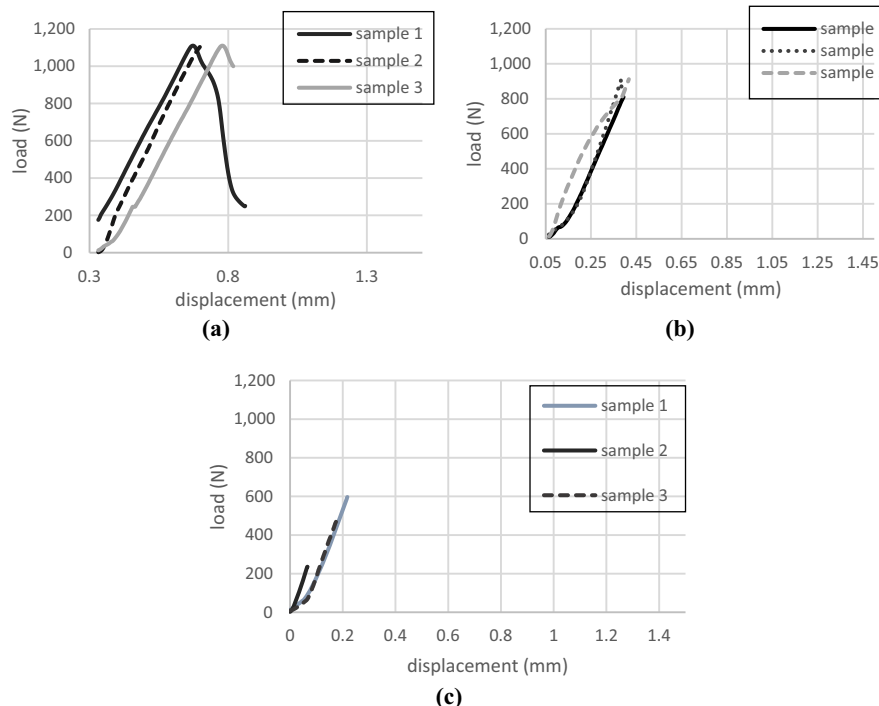


Figure 8 Load-displacement curves of the samples were bonded at 300°C for (a) 15 min (b) 60 min (c) 120 min



The morphology of the fracture surface shown in Figure 10 related to that of the bonded sample for 120 min within which the ε -phase is the only phase in the region of bonding. The fracture surface consists of sugar-like grains, voids, and gray phase. As shown in the figure, fracture took place in the interface of the ε /Cu layer. The EDS analysis results indicated that the sugar-like grains are similar to the ε -phase, and the substrate (gray phase) is close to copper.

Discussion

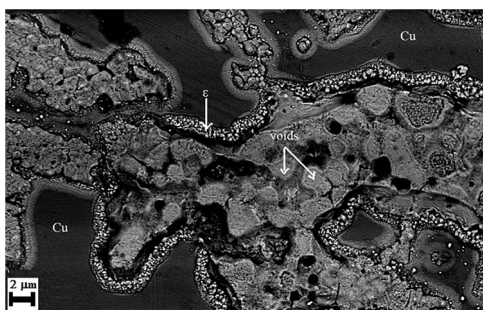
The phase transformations that were observed during this research are in agreement with observations made in previous TLP bonding studies that were conducted to investigate copper-tin systems. Typically, prior to the total consumption of the interlayer, two adjacent layers of intermetallic compounds (namely, the η -phase and the ε -phase) form at the interface. The η -phase exhibits scallop-like morphology, while the ε -phase has formed between the η -phase and the substrate as a very thin undulated layer. Upon the conversion of the interlayer, the ε -phase grows by consuming the η -phase and copper until the bonding region turns into the ε -single phase.

In the case of the phase formation mechanism, the scallop-shaped nature of the η -phase is one of the main reasons that the Sn interlayer was converted into intermetallic compounds in a relatively short period of time. According to previous studies, the scallops were found to have grooves between them that extend all the way to the ε /Cu interface. As the ε -phase is very thin, these grooves act as fast diffusion and dissolution paths of Cu into molten Sn (Bader *et al.*, 1995; Görlich *et al.*, 2005; Kim and Tu, 1996).

Also based on prior investigations that have been carried out by electron microscope studies, the wave-like morphology of the ε -phase has been attributed to the different crystalline orientation of the base metal (Shang *et al.*, 2009).

The ε -phase is formed via solid-state diffusion, in which both Cu and Sn atoms diffuse to one another, but the diffusivity of Cu is three times as fast as that of Sn. This imbalanced migration of diffusing species results in void formation in the ε -phase. Some researchers have attributed these voids to the Kirkendall effect. According to studies that have been conducted by Oh (1994), the diffusion coefficient of copper in the ε -phase at 125°C is three times that of tin. However, in some studies, these voids have been attributed to the presence of impurities in the base metal of the copper (Laurila *et al.*, 2005; Paul, 2004).

Figure 10 Fracture surface of the single-phase sample of ε



With regard to the mechanical properties, intermetallic compounds are very brittle, and the intermetallic compounds of the Cu-Sn system were found to be particularly brittle (Dirnfeld and Ramon, 1990). In this study, the microhardness results also indicated that the intermetallic compounds have a much higher hardness than the substrate. This is due to the fact that the bonds in IMCs are partially covalent and therefore oriented (Bader *et al.*, 1995). In addition, according to the shear test and Fractography, when the whole interlayer turned into intermetallic compounds, it caused the strength to decrease. This heterogeneous plasticity between the base metal and the bonding region resulted in stress concentration near the interface, which is why fracture occurred there.

Conclusion

This investigation into TLP bonding in the Cu-Sn system at 300°C for time durations ranging from 15 to 120 min has yielded the following results:

- Before coming into contact with itself from the two original interfaces, the η -phase exhibits scallop-shaped morphology.
- In the early stages of the bonding process, the growth rate of the η -phase is far higher than that of the ε -phase.
- When the interlayer is completely consumed, the ε -phase continues to grow at the expense of the η -phase and copper until all the η -phase disappears.
- The microhardness results show that the hardness of the interface which contains intermetallic compounds is greater than that of the base metal. Furthermore, the hardness number of the η -phase is higher than that of the ε -phase. The hardness numbers of the η -phase and the ε -phase are 894 and 689 HV, respectively.
- The shear strength decreased when the interlayer was fully consumed. Moreover, at the point at which it is converted into ε -phase only, the strength of the bonded samples exhibits its minimum value.

References

- Bader, S., Gust, W. and Hieber, H. (1995), "Rapid formation of intermetallic compounds by interdiffusion in the Cu-Sn and Ni-Sn systems", *Acta Materialia*, Vol. 43, pp. 329-337.
- Bartels, F., Morris, J., Dalke, G. and Gust, W. (1994), "Intermetallic phase formation in thin solid-liquid diffusion couples", *Journal of Electronic Materials*, Vol. 23 No. 8, pp. 787-790.
- Bernstein, L. (1966), "Semiconductor joining by the solid-liquid-interdiffusion (SLID) process", *Journal of the Electrochemical Society*, Vol. 113 No. 12, pp. 1282-1288.
- Bosco, N.S. and Zok, F.W. (1998), "Strength of joints produced by transient liquid phase bonding in the Cu-Sn system", *Acta Materialia*, Vol. 53 No. 7, pp. 2019-2027.
- Choudhury, S.F. and Ladani, L. (2016), "Local shear stress-strain response of Sn-3.5Ag/Cu solder joint with high fraction of intermetallic compounds: experimental analysis", *Journal of Alloys and Compounds*, Vol. 680, pp. 665-676.
- Chu, K., Sohn, Y. and Moon, C. (2015), "A comparative study of Cu/Sn/Cu and Ni/Sn/Ni solder joints for low temperature

- stable transient liquid phase bonding”, *Scripta Materialia*, Vol. 109, pp. 113–117.
- Deng, X. and Chawla, N. (2004), “A study on the bonding process of Cu bump/Sn/Cu bump bonding structure for 3D packaging applications”, *Acta Materialia*, Vol. 52 No. 14, pp. 4291–4303.
- Dirnfeld, S.F. and Ramon, J.J. (1990), “Microstructure investigation of Copper-Tin intermetallics and the influence of layer thickness on shear strength”, *Welding Journal*, Vol. 69 No. 10, pp. 373–377.
- Eagar, T.W. and Hoh, M.M. (1992), “Low temperature transient liquid phase (LTTLTP) bonding for Au/Cu and Cu/Cu interconnections”, *Journal of Electronic Packaging*, Vol. 114, pp. 443–447.
- Görlich, J., Schmitz, G. and Tu, K.N. (2005), “On the mechanism of the binary Cu/Sn solder reaction on the mechanism of the binary Cu/Sn solder reaction”, *Applied Physics Letters*, Vol. 86 No. 5, p. 053106.
- Huebner, H., Penka, S., Barchmann, B., Eigner, M., Gruber, W., Nobis, M., Janka, S., Kristen, G. and Schneegans, M. (2006), “Micro contacts with Sub-30 Mm pitch for 3D chip on chip integration”, *Microelectronic Engineering*, Vol. 83 Nos 11/12, pp. 2155–2162.
- Jung, D.H., Sharma, A., Mayer, M. and Jung, J.P. (2018), “A review on recent advances in transient liquid phase (TLP) bonding for thermoelectric power module”, *Reviews on Advanced Materials Science*, Vol. 53, pp. 147–160.
- Kim, H. and Tu, K. (1996), “Kinetic analysis of the soldering reaction between eutectic SnPb alloy and Cu accompanied by ripening”, *Physical Review B*, Vol. 53 No. 23, pp. 16027–16034.
- Klumpp, A., Merkel, R., Ramm, P., Weber, J. and Wieland, R. (2004), “Vertical system integration by using inter chip via and solid-liquid interdiffusion bonding”, *Japanese Journal of Applied Physics*, Vol. 43, pp. 3–4.
- Lapadatu, A., Simonsen, T.I., Kittilsland, G., Stark, B., Hoivik, N. and Dalsrud Guttorm Salomonsen, V. (2010), “Cu-Sn wafer level bonding for vacuum encapsulation of micro bolometers focal plane arrays”, *ECS. Trans.*, Vol. 33, pp. 73–82.
- Laurila, T., Vuorinen, V. and Kivilahti, J.K. (2005), “Interfacial reactions between lead-free solders and common base materials”, *Materials Science and Engineering: R: Reports*, Vol. 49 Nos 1/2, pp. 1–60.
- Lee, C.C. and Wang, C.Y. (1993), “Advances in bonding technology for electronic packaging”, *Journal of Electronic Packaging*, Vol. 115 No. 2, pp. 201–207.
- Lee, J., Hwang, H. and Rhee, M. (2015), “Reliability investigation of Cu/In TLP bonding”, *Journal of Electronic Materials*, Vol. 44 No. 1, pp. 435–441.
- Lee, B., Park, J., Jeon, S., Kwon, K. and Lee, H. (2010), “Study the bonding process of Cu bump/Sn/Cu bump bonding structure for 3D packaging applications”, *Journal of the Electrochemical Society*, Vol. 157 No. 4, pp. 420–424.
- Li, J.F., Agyakwa, P.A. and Johnson, C.M. (2011), “Interfacial reaction in Cu/Sn/Cu system during the transient liquid phase soldering process”, *Acta Materialia*, Vol. 59 No. 3, pp. 1198–1211.
- Liu, H., Wang, K., Aasmundtveit, K.E. and Hoivik, N. (2012), “Intermetallic compound formation mechanisms for Cu-Sn solid-liquid interdiffusion bonding”, *Journal of Electronic Materials*, Vol. 41 No. 9, pp. 2453–2462.
- Nai, S.M.L., Wei, J. and Gupta, M. (2009), “Interfacial intermetallic growth and shear strength of lead-free composite solder joints”, *Journal of Alloys and Compounds*, Vol. 473 Nos 1/2, pp. 100–106.
- Natzke, P. and Grossner, U. (2017), “Thin layer Ag-Sn transient liquid phase bonding using magnetron sputtering for chip to baseplate bonding”, *IEEE Transactions on Components and Packaging Technologies*, pp. 165–170.
- Oh, M. (1994), PhD Thesis, Lehigh University.
- Paul, A. (2004), PhD Thesis, Technical University of Eindhoven.
- Rodriguez, R.I., Ibitayo, D. and Quintero, P.O. (2013), “Kinetics of dissolution and isothermal solidification for gold-enriched solid-liquid interdiffusion (SLID) bonding”, *Journal of Electronic Materials*, Vol. 42 No. 8, pp. 2677–2685, doi:10.1007/s11664-013-2614-z.
- Shang, P.J., Liu, Z.Q., Pang, X.Y., Li, D.X. and Shang, J.K. (2009), “Growth mechanisms of Cu₃Sn on polycrystalline”, *Acta Materialia*, Vol. 57 No. 16, pp. 4697–4706.
- Tollefsen, T.A., Larsson, A. and Løvvik, O.L.E.M. (2012), “Au-Sn SLID bonding properties and possibilities”, *Metallurgical and Materials Transactions B*, Vol. 43 No. 2, pp. 397–405.
- van de Wiel, H.J., Vardøy, A.-S.B., Hayes, G., Fischer, H.R., Lapadatu, A. and Taklo, M.M.V. (2012), “Characterization of hermetic Wafer-Level Cu-Sn SLID bonding”, *4th Electronic System-Integration Technology Conference, ESTC, IEEE, Amsterdam*.
- William, W., Lee, C.C. and Member, S. (1998), “High temperature joints manufactured at low temperature”, *48th Electronic Components and Technology Conference (Cat. No. 98CH36206)*, IEEE Press, pp. 284–291.
- Zhao, X., Tian, Y. and Wang, N. (2013), “Solid-liquid interdiffusion in 3D package”, *14th International Conference on Electronic Packaging Technology, IEEE, Dalian*, pp. 143–147.

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