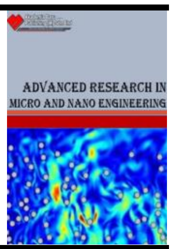
Penerbit Akademia Baru

Journal of Advanced Research in Micro and Nano Engineering

Journal homepage: https://www.akademiabaru.com/submit/index.php/armne/index

ISSN: 2756-8210



The Effect of Isothermal Aging on the Intermetallic Growth between SN100C Lead-Free Solders and ENIG Surface Finish

Dayang Izzah Nabilah Awang Azman[1], Saliza Azlina Osman[1,*], Pavithiran Narayanan[2], Yuji Kozutsumi[2]

[1] Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, 86400, Malaysia
[2] Nihon Superior (M) Sdn. Bhd., Free Industrial Zone Jelapanag 2, 30020 Ipoh, Perak, Malaysia

ARTICLE INFO

Article history:
Received 10 December 2023
Received in revised form 18 January 2024
Accepted 27 February 204
Available online 30 March 2024

Keywords:
Lead-free solder; reflow soldering; intermetallic compound (IMC); isothermal ageing; SN100C; ENIG

ABSTRACT

The selection of substrate material depends on solder joint requirements and will influence intermetallic compound (IMC) layer formation and reliability of the solder joints. Besides, using different solder materials can also affect the microstructure of IMCs formed during soldering and isothermal ageing process. This study investigated the effect of the IMC formation and microstructure evolution during reflow soldering and isothermal ageing using SN100C lead-free solders and ENIG surface finish. The characterization of the IMC formed during both reflow soldering and isothermal ageing in terms of the type, morphology, and thickness is then analyzed by using the Optical Microscope (OM), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX). The result reveals that there are two IMC formed at an interface between SN100C and ENIG which are $(Cu, Ni)_6Sn_5$ and $(Ni, Cu)_3Sn_4$ where $(Ni, Cu)_3Sn_4$ grows beneath $(Cu, Ni)_6Sn_5$. The thickness of the IMC formation in the SN100C/ENIG solder joint is also directly proportional to the ageing duration, indicating that the longer the time of the IMC exposed to high temperature affects the thickness of the IMC.

1. Introduction

Flip-chip interconnects are becoming more and more common as electronic packaging technology advances to meet the demands of high input/output (I/O) connect density and high operating frequency. Currently, flip-chip interconnect joints are used to package almost all large-scale integrated circuit (IC) chips [1]. Solder bumps are used in flip-chip technology as the interconnect between the chip and substrate. However, a substrate surface finish is essential to maintain the metal underplate's solderability. It plays a crucial role in determining the compound and intermetallic compound (IMC) characteristics formed at those interfaces, even altering the mechanical properties and microstructure of bulk solder joints [2].

Lead (Pb) is an example of a highly toxic heavy metal to living organisms and the environment even in small amounts [3,4]. Thus, due to environmental concerns, the Restriction of Hazardous

* *Corresponding author.*
E-mail address: salizaz@uthm.edu.my

https://doi.org/10.37934/armne.17.1.6975

Substances (RoHS) has legislated on the use of solder. Therefore, to comply with the RoHS regulations, the use of lead (Pb) in manufacturing printed circuit boards (PCBs) has been prohibited in Europe since July 2006. As a result, finding an appropriate Pb-free surface finish on a PCB is one of the key issues for developing Pb-free packaging systems [5]. The switch to lead-free soldering has made the surface finish requirements an even more crucial factor in manufacturing printed circuit boards today. The electroless nickel/immersion gold (ENIG) surface finish continues to grow as a popular option in electronic packaging even though various alternative surface finishes have been developed over the years. ENIG offers a uniformly flat surface finish, excellent solder attachment process control, and high performance [5,6]. However, given the significant volatility in the price of precious metals and the ongoing demand for better products at lower prices, manufacturers must look for ways to cut costs without compromising quality. Despite the thin layer of gold metal on ENIG surfaces, the thin gold layer adds a prohibitively high premium to the finishing [6,7]. In addition, ENIG finish has been discovered to produce embrittlement by forming (Au, Ni)Sn_4 at the interface during the isothermal ageing, which may damage the integrity of the solder connection [6,8].

In electronic packaging, good metallurgical bonding depends on the soldering reaction between solders and conductor metals during the soldering process. The interfacial IMC produced by the chemical reaction between the two components achieves metallurgical bonding between the solder and substrate [9]. However, the overgrowth of the interfacial IMC layer would eventually reduce the durability of the solder junction because it is inherently brittle and prone to structural flaws [10,11]. The formation of the interfacial reaction products plays a major effect on the reliability of solder joints as the properties of functional materials are significantly different depending on the thickness [12,13]. Due to the formation of IMC in the joints and the accelerated degradation of the solder alloys, solder joints are one of the most important parts of electronic device assemblies whose reliability is a concern at high operating temperatures [14].

The impact of IMC thickness on the structural integrity of solder joints has been the top subject of discussion. Mechanical characteristics like tensile and shear strength directly impact solder joints' dependability and integrity [14,15]. Understanding the solder-substrate metallization reaction is another crucial element of solder joint processing. It plays a significant role as it provides a protective coating on the surface of a printed circuit board (PCB). The surface finish prevents oxidation, corrosion and other environmental factors from occurring on the copper surfaces. The excessive growth of this intermetallic layer may lead to the degradation of solder joint reliability. Still, the morphology of the intermetallic layer after soldering and subsequent solid-state thermal processes may also affect the reliability of the solder joint [16]. Therefore, the effect on the intermetallic compound formation microstructure between SN100C lead-free solder and ENIG surface finish during reflow soldering and isothermal ageing process was investigated.

2. Methodology

The ready-made ENIG substrate was prepared by implementing the flux on the top surface and solder paste was arranged on the top of flux/substrate. The solder paste material used is SN100C, which consists of Sn-0.7Cu-0.05Ni-0.009Ge. The package was reflowed at 250°C using a conventional oven for 20 minutes and then cooled to room temperature. The joining process to form the solder joint is stated in the Joint Electron Device Engineering Council (JEDEC) standard of JESD22-B102E. After that, the package was subjected to isothermal ageing treatment at 150°C for a different ageing duration from 250 to 1000 hours. The isothermal ageing temperature has complied with the high-temperature storage test stated in JEDEC standard (JESD22-A103C). Top surface and cross-section characterization analyses will be investigated. The cross-section samples were mounted in the epoxy resin, followed by metallographic grinding and polishing techniques to remove unwanted materials from the surface to obtain the desired result. As for the top surface samples analysis, the samples were etched into a solder removal solution to expose the interfacial microstructure. The characterization of interfacial reaction after reflows and isothermal ageing process at the solder joint interface will be carried out by 3D morphology and cross-sectional examination of intermetallics was determined by selectively etching solution and using the Optical Microscope (OM), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX).

3. Results

3.1 Top Surface Examination

After reflow soldering, the immersion gold layer dissolved into the molten Sn-0.7Cu-0.05Ni-0.009Ge solder paste, exposing the nickel layer to the solder. Previous research has emphasized the importance of nickel layer, which serves as a barrier for preventing the inter-diffusion of copper and the solder [17,18]. As a result, the intermetallic layer was formed between the substrate and the molten solder with different types and grain sizes of intermetallic morphology. Figure 1 shows the top view images of the IMC morphology for the SN100C/ENIG joints reflowed under various isothermal ageing durations. The IMC morphology in SN100C/ENIG solder joints varies with the heating factors under a Scanning Electron Microscope (SEM). Energy Dispersive X-ray (EDX) spectrum analysis confirmed that the IMCs formed between the solder and ENIG were $(Ni, Cu)_3Sn_4$, Ni_3Sn_4, Ni_2Sn, $(Cu, Ni)_6Sn_5$ and Cu_6Sn_5. Besides that, an Au element was still detected at the IMC interface, indicating that not all of the gold layer dissolved into the molten solder within the ageing duration. After the reflow soldering process, the IMCs comprised a flake-like $(Ni, Cu)_3Sn_4$ and needle-like scallop Ni_3Sn_4. The Ni_3Sn_4 IMC morphology is thin and complies with the study made by Hsu *et al.,* [19], where Ni_3Sn_4 morphology is described as a continuous thin layer.

During isothermal ageing after 250 hours of exposure, a prismatic-shaped Cu_6Sn_5 IMC and chunk-like (Cu, Ni)6Sn5 were also formed at the interface between the SN100C/ ENIG solder joint. The difference in the IMC morphology was caused by the Ni atoms participating in the Cu_6Sn_5. The Ni in the solder alloy converts the composition of the interfacial IMC on the Cu substrate from Cu_6Sn_5 to $(Cu, Ni)_6Sn_5$, which explains the decrease in the IMC grain size. The similarity in the atomic sizes between Cu and Ni allows the Ni atoms to replace Cu atoms in the IMCs during the reflow and ageing in the solder joints. Furthermore, the increase of an atomic concentration gives more nucleation sites for $(Cu, Ni)_6Sn_5$ causing the IMC grain size of $(Cu, Ni)_6Sn_5$ to be smaller than Cu_6Sn_5. In contrast, when the concentration of Cu in the solder was significantly higher than Ni, no Ni element was found in the IMC. Since the limited number of Ni atoms that could participate in the nucleation of IMC the number of nuclei reduced and the grain size of the IMC increased as the Cu content of the solder alloy increased. Besides that, in the Cu-Ni-Sn ternary system, the formation of the $(Cu, Ni)_6Sn_5$ and $(Ni, Cu)_3Sn_4$ IMC is based on Cu_6Sn_5 and Ni_3Sn_4, where both $(Cu, Ni)_6Sn_5$ and $(Ni, Cu)_3Sn_4$ are claimed to be the stable one [20]. After the next 500 hours of ageing duration, the Ni_3Sn_4 IMC that was detected at the early ageing duration is no longer detected, as a result of the increase in the amount of Cu atoms in the solder where all the Ni_3Sn_4 IMC transforms to be $(Ni, Cu)_3Sn_4$. At the 1000-hour ageing duration, the flake-like $(Ni, Cu)_3Sn_4$ is also observed to transform into prismatic-like with the increases of the ageing duration or Cu content. It is also can be observed that no $(Cu, Ni)_6Sn_5$ detected as the $(Cu, Ni)_6Sn_5$ IMC may have stopped growing while the $(Ni, Cu)_3Sn_4$ IMC grew extensively covering most of the interfacial area. This may be caused by the Cu concentration of the $(Ni, Cu)_3Sn_4$ being lower than the $(Cu, Ni)_6Sn_5$. Therefore, it can be said that the Cu concentration decreases while forming (Cu, Ni)$_6$Sn$_5$, which then results in the formation or also in the increases of the size of the (Ni, Cu)$_3$Sn$_4$, aligned with the research made by Yang *et al.,* [21].

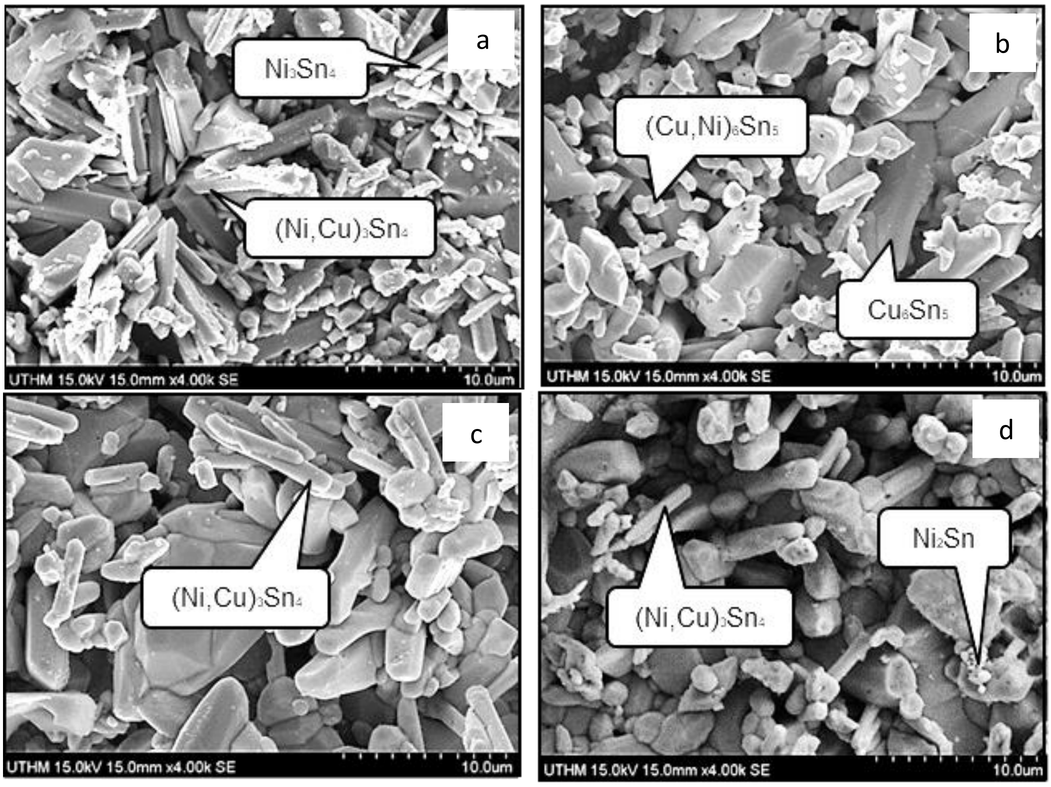


Fig. 1. Scanning electron microscopy view of SN100C solder with magnification 4000x (a) 0 hour; (b) 250 hours; (c) 500 hours; and (d) 1000 hours

3.2 Cross-Section Examination

Figure 2 shows the cross-section image of SN100C and ENIG solder joint analyzed by using the SEM. Consistent with the top surface examination, it was observed that (Cu, Ni)$_6$Sn$_5$ was the first layer formed during the reflow soldering process till after a certain time, (Ni, Cu)$_3$Sn$_4$ starts to grow beneath the (Cu, Ni)$_6$Sn$_5$. This IMC type has been approved by using the EDX spectrum analysis. The thickness of the IMC is also determined in Table 1 below, where the mean thickness of each IMC layer is 3.19µm, 3.23 µm, and 3.31 µm after 250h, 500h and 1000h ageing, respectively. The thickness of the IMC layer in thermal ageing can also be expressed theoretically by the diffusion coefficient and the ageing duration, where the diffusion coefficient can be defined by the pre-exponential diffusion constant, apparent activation energy, gas constant, and absolute temperature [22–24]. Therefore, it can be seen from Table 1 that the average thickness of the IMC layer against the square root of time at 150°C indicates that the IMC thickness is proportional to the ageing duration. It also can influence the formation of the IMC by adequately selecting the solder profile. Other than that, the density of impurity atoms and defects increases the metal's electrical resistivity at a given temperature. The IMC at the interface as well as the IMC precipitates in the solder during reflow may be the most relevant element. It is possible that when the number of reflow times also increased, the electrical resistivity of ball grid array (BGA) packages decreased since IMC has a higher resistivity than metal.

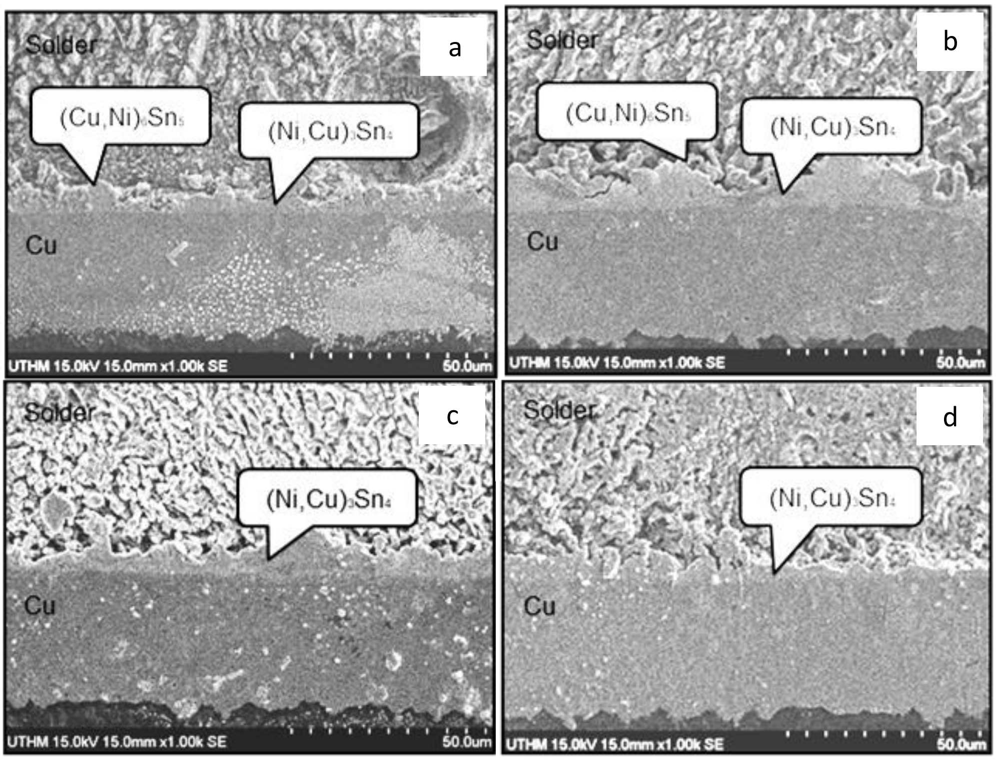


Fig. 2. Scanning electron microscopy view of SN100C solder with magnification 1000x (a) 0 hour; (b) 250 hours; (c) 500 hours; and (d) 1000 hours

Table 1
The values of Reynolds number and velocity

Ageing duration (hours)	IMC thickness, T (µm)					
	T_1	T_2	T_3	T_4	T_5	T_A
0	3.17	3.17	2.78	3.08	2.88	3.02
250	3.27	3.17	3.17	3.17	3.17	3.19
500	3.27	3.27	3.17	3.27	3.17	3.23
1000	3.27	3.27	3.27	3.37	3.37	3.31

4. Conclusions

In conclusion, the IMC that formed at the SN100C/ENIG solder joint are $(Ni, Cu)_3Sn_4$, Ni_3Sn_4, Ni2Sn, $(Cu, Ni)_6Sn_5$ and Cu_6Sn_5, where $(Ni, Cu)_3Sn_4$ and $(Cu, Ni)_6$Sn5 are the stable versions of Ni_3Sn_4 and Cu_6Sn_5. The $(Cu, Ni)_6Sn_5$ formed as the first layer and $(Ni, Cu)_3Sn_4$ grew just beneath the $(Cu, Ni)_6Sn_5$ at a certain period of isothermal ageing. The thickness of the IMC formation in the SN100C/ENIG solder joint is also directly proportional to the ageing duration due to the longer duration exposed to the high temperature.

Acknowledgement
This research was supported by Ministry of Higher Education (MOHE) through Fundamental Research Grant Scheme (FRGS/1/2019/TK03/UTHM/02/6), and facilities provided by Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia. Special thank you to Nihon Superior (M) Sdn. Bhd as a research collaborator.

References

[1] Sha, Chu-Hsuan, and Chin C. Lee. "Demonstration of silver micro-joints for flip-chip interconnect." *Microelectronic engineering* 99 (2012): 11-17. https://doi.org/10.1016/j.mee.2012.04.038

[2] Zhengrong, Chen, Zhou Jianwei, Fu Xingming, and Lee Jaisung. "Pad finish related board-level solder joint reliability research." In *2010 11th International Conference on Electronic Packaging Technology & High Density Packaging*, pp. 1039-1042. IEEE, 2010. https://doi.org/10.1109/ICEPT.2010.5582714

[3] Thotagamuge, Roshan, Muhammad Raziq Rahimi Kooh, Abdul Hanif Mahadi, Chee Ming Lim, Masanizan Abu, Abigail Jan, Alifatul Haziqah Abu Hanipah, Yong Yung Khiong, and Amanina Shofry. "Copper modified activated bamboo charcoal to enhance adsorption of heavy metals from industrial wastewater." *Environmental Nanotechnology, Monitoring & Management* 16 (2021): 100562. https://doi.org/10.1016/j.enmm.2021.100562

[4] Lokman, Nurul Fariha, Nurul Ain Shafiqah Anuar, Suhaimi Abdul-Talib, Tay Chia-Chay, Ahmad Ashrif Abu-Bakar, and Sharifah Abdullah. "Isotherm, Characterisation and Regeneration Studies for the Adsorption of Pb (II) Ions in Water." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 29, no. 3 (2023): 175-184. https://doi.org/10.37934/araset.29.3.175184

[5] Yoon, Jeong-Won, and Seung-Boo Jung. "Effect of immersion Ag surface finish on interfacial reaction and mechanical reliability of Sn–3.5 Ag–0.7 Cu solder joint." *Journal of Alloys and Compounds* 458, no. 1-2 (2008): 200-207. https://doi.org/10.1016/j.jallcom.2007.04.014

[6] Wang, Tong Hong, Chung-Hung Tsai, and Yi-Shao Lai. "Effect of the combination of surface finishes and solder balls on JEDEC drop reliability of chip-scale packages." *Microelectronic engineering* 98 (2012): 1-5. https://doi.org/10.1016/j.mee.2012.05.001

[7] Long, Ernest, and Lenora Toscano. "Electroless Nickel/Immersion Silver—A new surface finish PCB applications." *Metal Finishing* 111, no. 1 (2013): 12-19. ttps://doi.org/10.1016/S0026-0576(13)70171-5

[8] C. F. Coombs Jr, *Printed circuits handbook*. McGraw-Hill Education, 2008.

[9] Vidyatharran, K., MA Azmah Hanim, T. T. Dele-Afolabi, K. A. Matori, and O. Saliza Azlina. "Microstructural and shear strength properties of GNSs-reinforced Sn-1.0 Ag-0.5 Cu (SAC105) composite solder interconnects on plain Cu and ENIAg surface finish." *Journal of Materials Research and Technology* 15 (2021): 2497-2506. https://doi.org/10.1016/j.jmrt.2021.09.067

[10] Liu, Wen, and Dusan P. Sekulic. "Capillary driven molten metal flow over topographically complex substrates." *Langmuir* 27, no. 11 (2011): 6720-6730. https://doi.org/10.1021/la201091u

[11] Dele-Afolabi, T. T., MA Azmah Hanim, O. J. Ojo-Kupoluyi, and R. Calin. "Impact of different isothermal aging conditions on the IMC layer growth and shear strength of MWCNT-reinforced Sn–5Sb solder composites on Cu substrate." *Journal of Alloys and Compounds* 808 (2019): 151714. https://doi.org/10.1016/j.jallcom.2019.151714

[12] Lin, Yu-Wei, and Kwang-Lung Lin. "Nucleation behaviors of the intermetallic compounds at the initial interfacial reaction between the liquid Sn3. 0Ag0. 5Cu solder and Ni substrate during reflow." *Intermetallics* 32 (2013): 6-11. https://doi.org/10.1016/j.intermet.2012.07.035

[13] Naning, Fatin Hana, Syed Abdul Malik, and Hafizul Fahri Hanafi. "Isotherm Behaviour of P3OT, P3HT and PCBM Langmuir Layer on Ionic Subphase." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 29, no. 3 (2023): 168-174. https://doi.org/10.37934/araset.29.3.168174

[14] Amalu, Emeka H., and N. N. Ekere. "Damage of lead-free solder joints in flip chip assemblies subjected to high-temperature thermal cycling." *Computational materials science* 65 (2012): 470-484. https://doi.org/10.1016/j.commatsci.2012.08.005

[15] Chauhan, Preeti, Maik Mueller, Michael Osterman, and Michael Pecht. "Impact of thermal aging on the thermal fatigue durability of Pb-free solder joints." In *3rd Electronics System Integration Technology Conference ESTC*, pp. 1-10. IEEE, 2010. https://doi.org/10.1109/ESTC.2010.5642908

[16] Simona, Partinova. "Comparative analysis of surface finishes of printed circuit boards." *Восточно-Европейский журнал передовых технологий* 1, no. 5 (61) (2013): 64-68.

[17] Wang, S. J., and C. Y. Liu. "Study of interaction between Cu-Sn and Ni-Sn interfacial reactions by Ni-Sn3. 5Ag-Cu sandwich structure." *Journal of electronic materials* 32 (2003): 1303-1309. https://doi.org/10.1007/s11664-003-0027-0

[18] M. A. R. Adawiyah, O. S. Azlina, N. A. Fadil, S. R. Aisha, and M. . A. Hanim, “Electroless and Immersion Plating Process towards Structures and IMC Formation,” *Int. J. Eng. Technol.*, vol. 8, no. 6, pp. 2558–2570, 2016 https://doi.org/10.21817/ijet/2016/v8i6/160806210

[19] Lee, Hwa-Teng, Ming-Hung Chen, Huei-Mei Jao, and Chin-Jui Hsu. "Effect of adding Sb on microstructure and adhesive strength of Sn-Ag solder joints." *Journal of electronic materials* 33 (2004): 1048-1054. https://doi.org/10.1007/s11664-004-0034-9

[20] Liu, Yang, Fenglian Sun, and Yang Liu. "Characterization of interfacial IMCs in low-Ag Sn–Ag–xCu–Bi–Ni solder joints." *Journal of Materials Science: Materials in Electronics* 24 (2013): 290-294. https://doi.org/10.1007/s10854-012-0741-6

[21] Huang, M. L., and F. Yang. "Solder size effect on early stage interfacial intermetallic compound evolution in wetting reaction of Sn3. 0Ag0. 5Cu/ENEPIG joints." *Journal of Materials Science & Technology* 31, no. 3 (2015): 252-256. https://doi.org/10.1016/j.jmst.2015.01.003

[22] Suganuma, Katsuaki. "Advances in lead-free electronics soldering." *Current Opinion in Solid State and Materials Science* 5, no. 1 (2001): 55-64. https://doi.org/10.1016/S1359-0286(00)00036-X

[23] Kim, Young-Sun, Keun-Soo Kim, Chi-Won Hwang, and Katsuaki Suganuma. "Effect of composition and cooling rate on microstructure and tensile properties of Sn–Zn–Bi alloys." *Journal of alloys and compounds* 352, no. 1-2 (2003): 237-245. https://doi.org/10.1016/S0925-8388(02)01168-4

[24] Zhang, Lili, Si Chen, Peng Sun, Zhaonian Cheng, and Johan Liu. "An aging study of intermetallic compounds formation in Sn-0.4 Co-0.7 Cu." In *2007 International Symposium on High Density packaging and Microsystem Integration*, pp. 1-5. IEEE, 2007. https://doi.org/10.1109/HDP.2007.4283623