

Effect of Germanium addition to Sn3.5Ag Lead Free Solder System for Overall BGA Package Robustness Improvement

Eu Poh Leng^{1&2}, Wong Tzu Ling^{1&2}, Min Ding², Nowshad Amin¹, Ibrahim Ahmad¹, Tay Yee Han³ and A.S.M.A. Haseeb³

¹Faculty of Engineering, Department of Electrical, Electronics & System,
National University of Malaysia
43600 Bangi, Selangor, Malaysia

Tel: 603-89216322 Fax: 603-89216146

²Freescall Semiconductor, (M) Sdn. Bhd.

No. 2, Jalan SS 8/2 Free Industrial Zone

Sungei Way Petaling Jaya 47300

Tel: 603-78823790

³Faculty of Engineering, Department of Materials Engineering,
University Malaya Malaysia
KL, Selangor, Malaysia

Email: r38158@freescall.com

Abstract

A study was conducted on BGA lead-free C5 solder joint system to assess the effect of Germanium addition to Sn3.5Ag solder alloy through comparison study of Sn3.5Ag vs. Sn3.5AgGe. The main objective of this study is to find a way to resolve solder surface oxidation after thermal processes, while determining if there's any adverse effect on the solder joint by Germanium addition. The result of this study showed that addition of Germanium in Sn3.5Ag C5 solder system resolved solder surface oxidation after thermal processes, without any negative impact to the solder joint and solderability. Experimental works were carried out to observe the melting properties and solder surface morphology by Differential Scanning Calorimetry (DSC) and SEM. Solder surface oxidation was measured by EDX. Shear and pull strength was measured by Dage which is representative of the intermetallic (IMC) strength between the C5 solder sphere and Cu/Ni/Au pad finishing. Solderability test was conducted per Jedec standard. Tray and Packaging Drop Tests were done to gauge solder joint performance against impact force. A comprehensive study was done to study the effect of microstructure and interface intermetallic of both solder system at ambient, high temperature storage (HTS) at 150°C for 24, 48, 96, 168, 504 and 2000 hours and multiple reflow of 1x, 2x, 3x, 6x towards the joint integrity. In each read point, Sn3.5AgGe has significantly higher ball shear and ball pull strength. EPMA microstructure analysis after cross-sectioning on bulk solder and IMC revealed traces of Germanium that contributed to the significant increase in ball shear and ball pull strength, while did not cause any bulk solder and IMC morphology changes. Both solderability and drop test passed. In conclusion, addition of Germanium in Sn3.5Ag lead-free solder is able to resolve surface oxidation problem after thermal processing, with improvement in solder joint strength for overall lead-free package robustness.

Keywords: Germanium, BGA packaging, lead-free C5, surface oxidation, Intermetallic; Sn3.5Ag, Shear and pull strength.

Introduction

The introduction of lead-free solder in recent years has spurred the development of new processes and materials. The effort to replace lead-based solder

with lead-free solder was because of the toxicity of lead that is hazardous to human and the environment.

One of the problems that the Semiconductor industry faces with lead-free solder ball is solder surface oxidation after thermal processing. This is

due to the formation of Tin Oxide which is more prominent in lead-free solder with > 90% of Tin in most of the lead-free alloys. The oxidation normally appears yellowish or brown or black color, depending on the oxidation level. Whatever the level may be, such discoloration is not acceptable to customers due to the concern of possible board mounting solder ability failure. Also, such discoloration may cause auto visual inspecting machine errors during component placement process at Surface Mount.

In the market, there have been some lead free solder doped with germanium. The low content of germanium shows remarkable anti-oxidation effect on the alloys. Besides, it shows excellent effect in relating to the solderability, strength, stability of composition and wettability. Moreover, some of the new solder has similar or higher performances than conventional lead solder ¹. In the previous works, the addition of germanium to a lead-free solder are combined with the IMC growth-suppressing element like Ni and strength-improving elements like Sb, Ni, Co, Fe, Mn, Cr and Mo. In this research, a new lead free solder alloy based on Sn-Ag system which contains a small amount of germanium is developed.

In this study, Sn3.5Ag doped with 75ppm Ge was being compared to conventional Sn3.5Ag solder alloy. The main objective is to resolve solder surface oxidation after thermal processes, while determining if there's any adverse effect on the solder joint by Germanium addition. Experimental works were carried out to observe the melting properties and solder surface morphology by Differential Scanning Calorimetry (DSC) and SEM. Solder surface oxidation was measured by EDX. Shear and pull strength was measured by Dage which is representative of the intermetallic (IMC) strength between the C5 solder sphere and Cu/Ni/Au pad finishing. Solderability test was conducted per Jedec standard. Tray and Packaging Drop Tests were done to gauge solder joint performance against impact force. A comprehensive study was done to study the effect of microstructure and interface intermetallic of both solder system at ambient, high temperature storage (HTS) at 150°C for 24, 48, 96, 168, 504 and 2000 hours and multiple reflow of 1x, 2x, 3x, 6x towards the joint integrity. In each read point, Sn3.5AgGe has significantly higher ball shear and ball pull strength. EPMA microstructure analysis after cross-sectioning on bulk solder and IMC revealed traces of Germanium that contributed to the significant increase in ball shear and ball pull strength, while did not cause any bulk solder and IMC morphology changes. The result of this study showed that addition of Germanium in Sn3.5Ag C5 solder system resolved solder surface oxidation after thermal processes. Also, addition of Germanium

helped to improve solder joint strength of Sn3.5Ag and did not impact solderability. In conclusion, addition of Germanium in Sn3.5Ag lead-free solder is able to resolve surface oxidation problem after thermal processing, with improvement in solder joint strength for overall lead-free package robustness.

2. Study Design

This study comprises 8 parts:

1. Solder balls melting properties measurement through Differential Scanning Calorimetry (DSC).
2. Solder ball surface morphology study through Scanning Electron Microscope (SEM).
3. Assembly and test of samples with TBGA substrates.
4. Solder surface oxide thickness measurement using EDX
5. Cold ball pull and ball shear measurement after assembly, after multiple reflow (1x, 2x, 3x, 6x) and after High Temperature Storage at 150 deg. C (24, 48, 96, 168, 504, 2000hrs).
6. Cross sectioning and etching for IMC and solder microstructure analysis.
7. Solderability test per Jedec standard (JESD22-B102D).
8. Tray drop test and packing drop test.

3. Subjects and Methods

3.1. Subjects

37.5x37.5mm 740TBGA with electrolytic Ni/Au pas finishing was used as test vehicle. This package was chosen due to smallest pad to ball ratio which represented the most stringent case in solder joint testing. Both solder alloys were supplied by the same vendor. Solder composition and test vehicle details are shown on Table 1.

Table 1. Details of package used in this study

Solder Ball Composition	96.5%Sn3.5%Ag and 96.5%Sn3.5%Ag Ge (75ppm)
Package Type	TBGA
Ball Count	740
Package Size	37.5x37.5mm
Ball Pitch	1.00mm
Ball Size	0.66mm
Solder Mask Opening Diameter	0.45mm
Solder Pad to Ball Diameter Ratio	0.68
Cold Ball Pull LSL	550g

3.2 Methods

3.2.1 Melting Properties

Melting properties of each solder type were tested with differential scanning calorimeter (DSC). DSC model *Metler Toledo 822e* was used and the method performed was heating at a rate of 5°C/min from 180-260°C. It is believed that melting properties affects the IMC growth as a larger melting range subjects the unit to a longer heating period that will encourage IMC growth. Therefore, it is important to understand the melting properties of each solder composition.

3.2.2 Solder Surface Morphology

Scanning Electron Microscope (SEM) was used to study solder ball surface morphology. The purpose is to check for presence of notches and channels which may trap contamination and prevent the dispense of flux during ball attachment and resulted in solder voids that may affect solder joint integrity.

3.2.3 Samples Preparation

Two lots of samples were assembled, where one lot was attached with Sn3.5Ag and the other lot with Sn3.5AgGe. Solders are being attached and reflowed on the TBGA substrate using Motorola Manufacturing System (MMS). Ramp-to-peak reflow profile was used in this study as displayed in Figure 1.

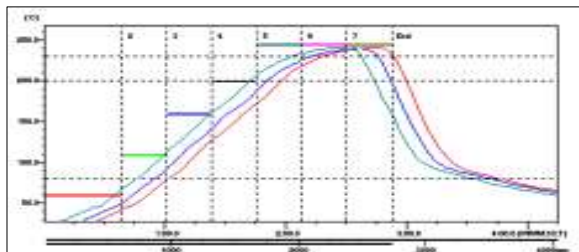


Figure 1. Ramp-to-peak reflow profile

3.2.4 Solder Surface Oxide Thickness Measurement

Solder surface oxide thickness measurement was done using EDX after the samples have completed assembly and test, including all thermal processes such as reflow, burn-in, data-retention-bake and moisture baking at test backend.

3.2.5 Cold Ball Pull (CBP) and Ball Shear (BS) Test

For the past few years, cold ball pull was found to be a more reliable outgoing metrology to gauge solder joint performance especially for lead-free products. Advantages of CBP were found to be 2 folds: 1. CBP test produces more IMC brittle

failures which is more stringent to differentiate the performance of different elements within the lead-free solder ball alloy and the solder pad; 2. CBP brittle failures represent a measurement of joint strength under dynamic load conditions and it correlates to drop test results.

In this study, both cold ball pull and ball shear test were carried out using Dage 4000 system for each study condition. Details of the CBP test and ball shear parameters are displayed in Table 2 and Table 3 respectively.

Table 2. CBP test speed & jaw size used

	Parameter
CBP Speed	5mm/sec
Jaw Size	0.76mm

Table 3. Ball shear test parameters & shear tool used

	Parameter
Land speed	300um/sec
Test height	40 um
Test speed	300 um/s
Threshold/test load	1000 g
Over travel	100 um
Fall back	10%
Shear Tool Face Width	650um

Sample size for ball pull and ball shear test is 10 units. For each unit, 8 outer corner balls were tested per sample with 2 balls at each corner of the sample. The corner balls were perceived to have the weakest joints strength as they have the longest distance from the package center point. The common possible failure modes are listed in Table 4.

Table 4. CBP & ball shear test failure modes

	CBP	Ball Shear
(Mode 1) Breaking in Bulk Solder		
(Mode 2) Brittle Failure at the IMC		
(Mode 4) Lifted Solder Pad		

3.2.6 Cross Section and Etching

Samples were mounted in cups using resin and left to harden overnight at room temperature. Then, the samples were cross-sectioned and polished to study the solder/ally interfaces after resin had hardened. The microstructure observation can be well observed under Olympus BH3-MJL Microscope. For some samples, the solders were chemically etched by 100% of hydrochloric acid (HCl) for the range between two to five hours. Top-view morphology was then examined by JSM-6390LV scanning electron microscope (SEM). Composition of the IMC was analyzed by EPMA.

3.2.7 Solderability Test

Solderability test was performed to assess the ability of component attachment to Printed Circuit Board (PCB). Sample size used is 15 samples for each lot. Prior to solderability test, all samples were stressed through steam aging with 100C/100%RH for 8 hours and followed by 1 hour baking at 125°C. The solderability test procedure is shown in Figure 2.

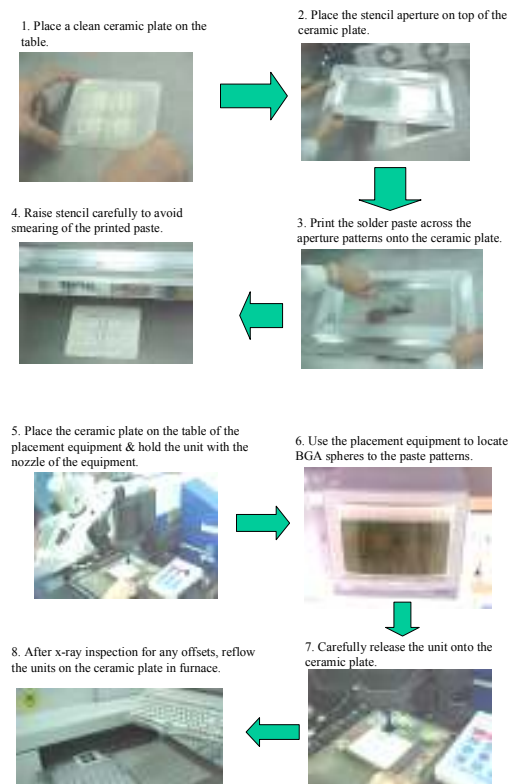


Figure 2. Solderability Test Procedure

After solderability reflow, units were removed from the ceramic plate. The balls were inspected under 30x scope for any of the following failure modes :

a. Satellite balls as shown in Figure 3:

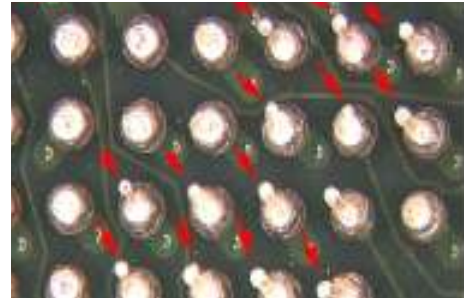


Figure 3. Satellite balls

b. Solder remain on ceramic plate

If there is any solder paste remained on the ceramic plate, this shows solder paste is not fully absorbed by the balls on the component which indicates non-wetting failure.

3.2.8 Tray Drop Test and Packing Drop Test

In this study, two types of package level drop tests were performed. They were tray drop test and packing drop test. The purpose was to assess the solder joint robustness against vibration & impact shock. Tray drop test was done to assess package solder joint integrity during handling in the production floor, while packing drop test is to assess the handling during product shipment and transportation to customers. This was done using center pedestal support trays. Both drop testings were performed to obtain drop till fail data. During drop tests, if there is any broken tray, it will be replaced to prevent tray chips from inducing any ball drop.

Figure 4 illustrates the tray drop test method while Figure 5 illustrates the packing drop test method.

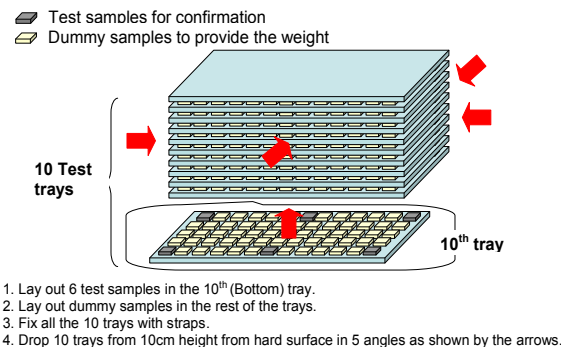


Figure 4. Schematic drawing of tray drop test

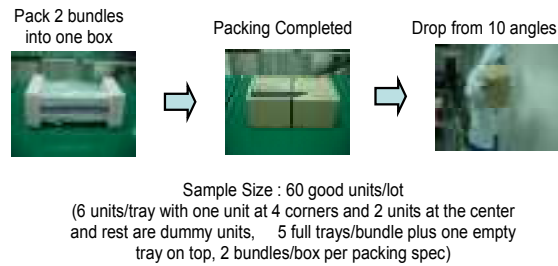


Figure 5. Schematic drawing of packing drop test

4. Results and Discussion

4.1 Melting Properties

Table 5 summarizes the results of DSC for both solder alloys, while the DSC graphs are displayed in Figure 5. Result shows that addition of 75ppm Ge did not change the melting behavior of Sn3.5Ag.

Table 5. Summary Result of the Melting Behavior

Solder Ball Type	Onset (°C)	Peak (°C)	Endset (°C)	Melting Range (°C)
Sn3.5Ag	221.19	222.88	224.65	3.46
Sn3.5AgGe	221.04	222.66	224.45	3.41

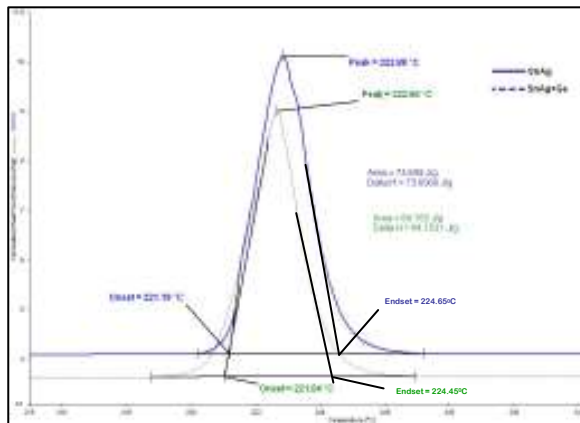


Figure 6. DSC graph for both alloys

4.2 Solder Surface Morphology

SEM images were taken at 1000x on the solder ball surface of Sn3.5Ag and Sn3.5AgGe to compare the alloy surface morphology. From the SEM images, there is no significant difference between these 2 alloys, though the dendrites on Sn3.5AgGe surface appears to be more nodule like. Nevertheless, both did not exhibit notches or pits or channels which may trap contaminant and prevent the dispense of flux during ball attachment and hence did not have risk of solder voids during ball attachment.

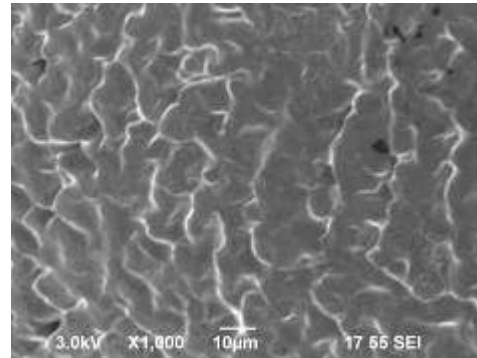


Figure 7. SEM image on solder ball surface of Sn3.5Ag alloy

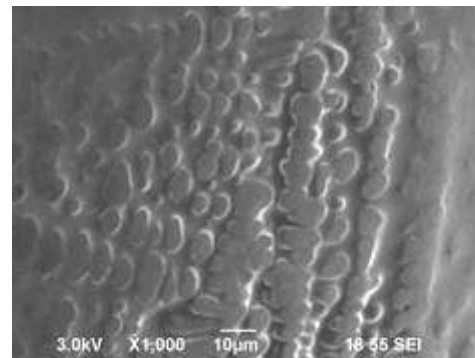


Figure 8. SEM image on solder ball surface of Sn3.5AgGe alloy

4.3. Solder Surface Oxide Thickness Measurement

In this test, the main purpose is to measure the oxide layer on solder surface after the samples had gone through assembly and test. Hence, EDX analysis with 5kV was used to ensure sampling depth was only on the very surface of the solder. Therefore, elements of Sn, Ag and Ge were not detected. EDX result showed that weight % of oxygen on Sn3.5Ag solder ball surface was 53.82% whereas Sn3.5AgGe had only 31.09%. It can be observed that Sn3.5Ag had much higher oxide thickness than Sn3.5AgGe.

After HTS 2000hrs, no oxidation can be seen on Sn3.5AgGe, while Sn3.5Ag had turned black due to severe oxidation as shown in Figure 9. Therefore, Ge addition to Sn3.5Ag was confirmed effective in reducing solder surface oxidation.

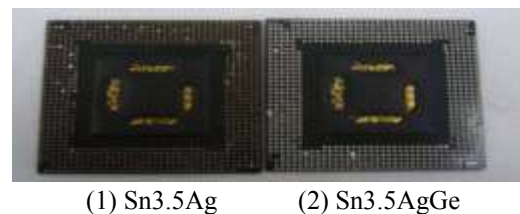


Figure 9. 2 alloys comparison after HTS 2000hrs.

4.4 Cold Ball Pull (CBP) and Ball Shear (BS) Test

Figure 11 and Figure 12 show the pull strength of both the alloy system after multiple reflow and high temperature storage, respectively. Generally two break modes were observed: 1. IMC brittle failure and 2. lifted pad (see figure 10).

Sn3.5AgGe showed higher pull strength in all stress conditions than Sn3.5Ag. One tail p-value for multiple reflow and HTS samples were $1.77\text{e-}06$ and $1.23\text{e-}09$ respectively, which was sufficient to infer that the pull strength of Sn3.5AgGe was significantly higher than Sn3.5Ag. After multiple reflow, both alloy systems showed constant pull strength which indicates the solder joint reliability. Besides, the fracture place of all solders mostly occurred in pad, which indicated strong solder joints.

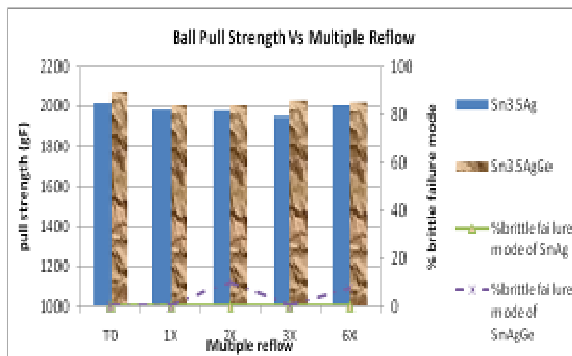
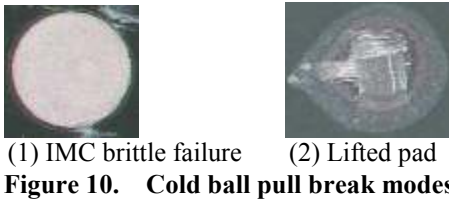


Figure 11. Pull strength and percentage of brittle failure after multiple reflow of 1x, 2x, 3x and 6x

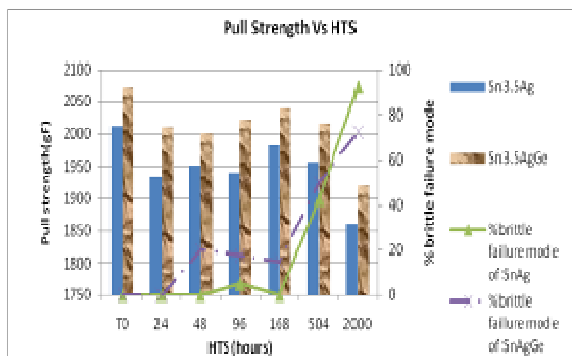


Figure 12. Pull strength and percentage of brittle failure after high temperature storage at 150 deg. C for 24, 48, 96, 168, 504 and 2000 hours.

Figure 14 shows the average shear strength of both solder systems at different multiple reflow. Both the alloys showed ductile failure mode in all the stress conditions (see figure 13). The shear strength of both alloys were fallen in the range of 1000-1100gF. It was observed that Ge addition to Sn3.5Ag has higher shear strength. The one-tail p value is $3.47\text{e-}06$ which indicated the shear strengths increased significantly by small amount of Ge.



Figure 13. Ductile failure mode was observed after ball shear test in all the test conditions

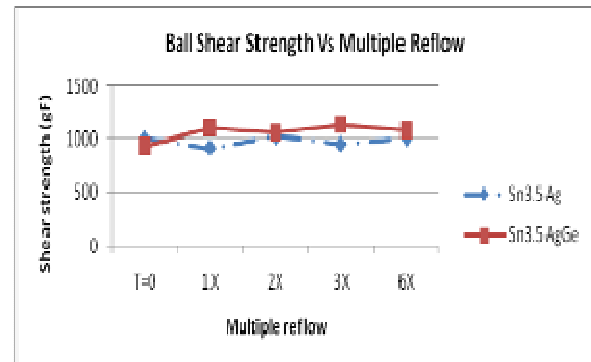


Figure 14. Ball shear strength with multiple reflow time of 1x, 2x, 3x and 6x

The same shear result was observed after high temperature storage (see Figure 15). Sn3.5AgGe was found to have higher shear strength at all stress conditions versus Sn3.5Ag.

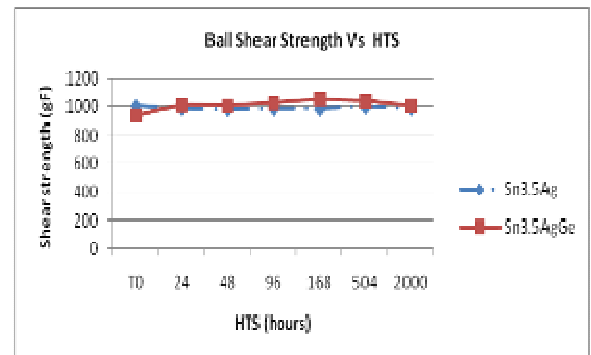


Figure 15. Ball shear strength with HTS time of 24, 48, 96, 168, 504 and 2000 hours

4.5 Cross Section and Etching

During solder reflow, inter metallic compound (IMC) is formed from chemical reaction between Sn in the solder and Ni in the solder pad, after the thin layer of Au on solder pad has diffused into the bulk solder. Essentially, IMC thickness is one of the major concerns to predict the solder joint reliability. A thin and continuous IMC layer is essential for good wetting and bonding. However, due to the inherent brittle nature of the IMC, thick IMC layer at the solder/substrate interface may degrade the reliability of the solder joint². The thicker the IMC layer at the interface, the lower the pull strength of the joint³. Part of this study was focused on IMC cross-sectioning measurement using high power scope of 100x and Image Analyzer to measure the IMC thickness.

Figure 16 and 17 show that IMC thickness trend of Sn3.5AgGe was comparable to Sn3.5Ag for all the stress conditions of multiple reflow and HTS. Although after multiple reflow the IMC thickness of Sn3.5AgGe was slightly lower than Sn3.5Ag, but the difference was less than 1µm, which is within the error of cross sectioning process.

For HTS, Figure 17 shows that IMC thickness grew rapidly from T0 to 100 hours. After HTS 100 hours, IMC grew at a slower rate. This is because at the beginning of thermal aging, the formation of IMC was controlled by reaction diffusion and the growth rate should be very high. When the layer reaches a certain thickness, the growth was controlled by grain boundary diffusion mechanism, hence IMC growth rate became slower⁴. As a whole, Ge did not influence the growth of the IMC thickness and retain the good reliability of the Sn3.5Ag solder.

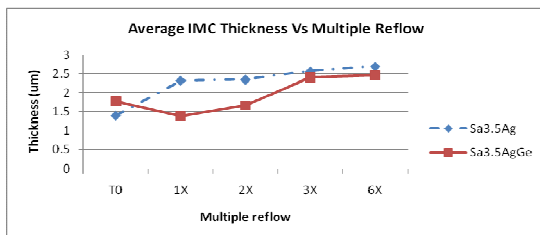


Figure 16. IMC after multiple reflow

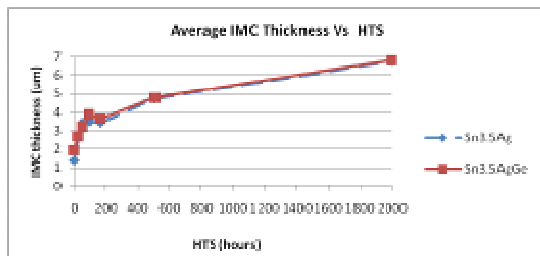


Figure 17. IMC after HTS at 150 deg. C

When solders comes in contact with a common metal substrate for a sufficient amount of time at a high enough temperature, formation is primarily a solid state diffusion process and thus depends highly on temperature and time. While solder is in a molten state, the solubility of the element from substrate into molten solder accelerates the rate of the intermetallic formation⁵.

Many works had been done on the growth of IMC during thermal aging. Such studies indicated that the growth of IMC in the Sn base solder/Cu interface followed the diffusion controlled mechanism with the value of n as 0.5. The IMC growth rate in thermal aging can be expressed as below⁶:

$$\delta = \delta_0 + k\sqrt{t}$$

where	δ	= thickness IMC at time t
	δ_0	= thickness IMC at t0
	k	= growth constant
		= $A \exp(-Q/RT)$
	A	= prefactor
	T	= absolute temperature
	R	= gas constant
	Q	= activation energy

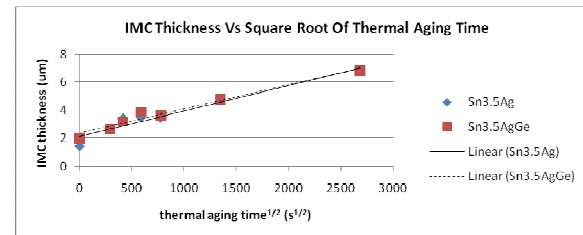


Figure 18. IMC thickness versus square root of thermal aging time.

Figure 18 shows that the IMC growth constant, k of Sn3.5AgGe is $1.818 \times 10^{-9} \text{ m}^2/\text{s}$ whereas for Sn3.5Ag is $2.00 \times 10^{-9} \text{ m}^2/\text{s}$. This result proved that Sn3.5Ag and Sn3.5AgGe had comparable IMC growth rate after thermal aging, hence implied that the IMC layer growth was not affected by the addition of Ge.

Figures 19 and 20 display the top view morphology changes in the interfacial IMC layer of Sn3.5Ag and Sn3.5AgGe solders on Cu/Ni/Au electrolytic finish after thermal aging and multiple reflowed. The IMC growth after HTS was more evident than the IMC growth after multiple reflow for both solder alloys. At T0, the IMC of both alloys appeared to be irregular and needle-like. After 2000hrs of thermal aging, the growth and coalescence of original IMC needles resulted in lateral thickening and ripening. Both solders

exhibited similar interfacial growth reactions after thermal aging.

EPMA microstructure analysis after cross-sectioning on bulk solder and IMC revealed traces of Ge that contributed to the significant increase in ball shear and ball pull strength, while did not cause any bulk solder and IMC morphology changes.

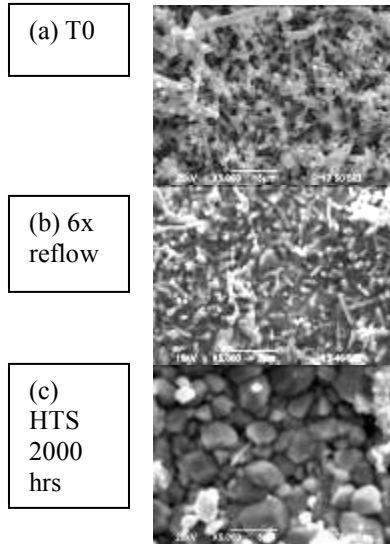


Figure 19. Top view of Sn3.5Ag IMC after solder etching (under SEM 5000x)

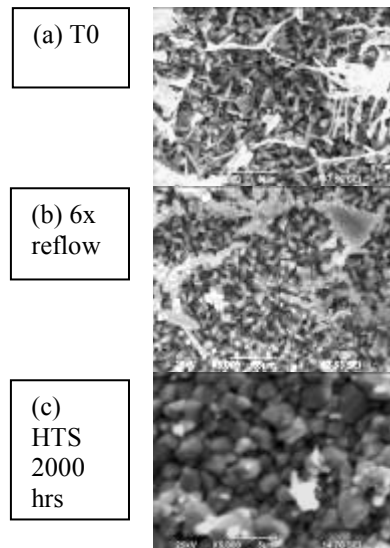


Figure 20. Top view of Sn3.5AgGe IMC after solder etching (under SEM 5000X)

4.6 Solderability Test

Both alloys passed solderability testing after 8hrs of steam aging.

Table 6. Solderability result.

Lot	Qty	Solderability
Sn3.5Ag	15 units	Pass
Sn3.5AgGe	15 units	Pass

4.7 Tray Drop Test and Packing Drop Test

30 units were tested in tray drop test while 60 units were tested in packing drop test. Both Sn3.5Ag and Sn3.5AgGe did not have any dropped balls in both of the drop tests.

Table 7. Drop tests result.

		Sn3.5Ag	Sn3.5AgGe
	Number of Samples Tested	Number of Dropped Ball	Number of Dropped Ball
Tray Drop Test	30	0	0
Packing Drop Test	60	0	0

5. Conclusions

The effect of Ge doping into Sn3.5Ag was thoroughly studied. In conclusion, Ge doping significantly reduced solder surface oxidation after thermal aging, while maintaining the solder melting behavior, solder surface morphology, IMC growth rate, solderability and drop tests performance. In terms of ball pull and ball shear result, Ge doping had demonstrated significant improvement in ball pull and ball shear strength, due to the traces of Ge in the bulk solder and IMC as shown through EPMA analysis. Overall, Ge doping in lead-free solder is able to resolve solder surface oxidation problem after thermal processing, with improvement in solder joint strength for overall lead-free package robustness.

Acknowledgments

We would like to acknowledge the great support of Freescale management and MOSTI for sponsoring the fund for this project. Our gratitude is also extended to Prof Dr Burhanuddin Yeop Majlis as the Chairman for this Sector of UKM. We would also like to thank Senju Corporation Japan and Mitsui Singapore for sponsoring the solder balls and providing technical advice in this study.

References

- [1] Habu, K., Takeda, N., Watanabe, H., Ooki, H., Abe, J., Saito, T., Taniguchi, Y. & Takayama, K. (1999). Development of Lead-free solder Alloys of the Ge doped Sn-Ag-Bi system. *Journal of IEEE*. 606-609.
- [2] Zhu, W.J., Liu, H.S., Wang, J. & Jin, Z.P. (2008). Formation of intermetallic compound (IMC) between Sn and Co substrate. *Journal of Alloys and Compounds*, **456**, 113-117.
- [3] Sang Won Jeong, Jong Hoon Kim, and Hyuck Mo Lee, "Effect of Cooling Rate on Growth of the Intermetallic Compound and Fracture Mode of Near Eutectic Sn-Ag-Cu/Cu Pad: Before and After Aging, *Journal of Electronic Materials*, Vol.33, No.12, 2004.
- [4] Yu, D.Q. & Wang, L. (2008). The growth and roughness evolution of intermetallic compounds of Sn-Ag-Cu/Cu interface during soldering reaction. *Journal of Alloys and Compounds*. **458**, 542-547.
- [5] Harper, C.A. (2000). *Electronic packaging and interconnection handbook*. 3rd Ed. McGraw Hill Publishers, United State of America.
- [6] Qi, L., Zhao, J., Wang, X. M. & Wang, L. (2004). The effect of Bi on the IMC growth in Sn-3Ag-0.5Cu solder interface during aging process, in Proceedings of Business of Electronic Product Reliability and Liability International Conference, 42-47.
- [7] Robert Sykes, Dage Precision Industries Ltd., Pull testing of solder balls on BGA and CSP packages without reflow