Effects of Gallium addition on the thermal properties and whiskers growth under electrical current stressing

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Abstract. This study investigates the effects of Gallium addition to the thermal behaviour and whiskers growth under electrical current stressing to the microstructure and intermetallic (IMCs) between solder and copper substrate. The samples were dipped using Sn-0.7Cu and Sn-0.7-0.05Ga solder and further continued with electromigration process for whiskers growth observation. The characterization were then analysed using Scanning Electron Microscopy (SEM) on the surface and intermetallic layer. From the observation, the addition of 0.05% Ga has lowered the melting point of Sn-0.7Cu-0.05Ga Copper and refined the microstructure. There is no indication of new phase form after 0.05%Ga addition. Furthermore, whiskers were observed to grow at both Sn-0.7Cu and Sn-0.7Cu-0.05Ga. However, the whiskers growth on both cathode and anode sides have been reduced with the Ga addition. It is also observed that the hardness increased with the addition of Ga element to the solder.

1 Introduction

Due to increasing environmental concerns, the microelectronics industries have been replacing Pb-containing solders with lead-free solder elements [1-5]. Among the most promising Pb-free candidates to replace the conventional SnPb includes Sn-0.7Cu [6-9]. The use of Sn-0.7Cu will enhance the growth of Sn whiskers [10-11]. Sn whiskers are an electrically conductive single or polycrystalline structure that spontaneously formed on the Sn coating. The issues of whiskers are they may grow long enough and cause short circuiting and interfere with other devices in application [12].

Several reports have studied the growth of Sn whiskers with the addition of this rare earth element. Nd has been added to the Sn-0.7Cu with the formation of Sn3Nd and cause the growth of tin whiskers [13]. Furthermore, Sn-Zn has been used to change the microstructure to the equiaxed grain that will incubate the whiskers growth using pulsed plating technique [14]. Moreover, Sn-2Bi has shown improvement in mitigating Sn whiskers growth by refining the grain structure and altering the microstructure from

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columnar to equiaxed grain structure [15]. This mitigating process is due to the releasing internal stress with the Bi addition.

Other than that, several method have been proposed to mitigate the whiskers formation such as annealing at 150°C for 1 hour, mitigating the whiskers formation by inserting the Ni nanocones, conformal coating as it can stop the whiskers from penetrating barrier and forming short, reduce the thickness of plating, and by controlling the environmental effects [16-19]. But the mechanism of whiskers growth and all these mitigation methods are still have not yet been fully understood.

The previous research have found that the electrical current stressing had effects on the whiskers growth and IMCs formation [12]. But there are limited study on the effect of Ga addition to the whiskers growth under electromigration in term of whiskers growth and IMCs refinement. In this study, we focus on the thermal, mechanical and microstructural properties of Ga addition which allow the reduction on the formation of whiskers.

2 Methodology

2.1 Raw Materials Preparation

The Sn-0.7Cu and Sn-0.7Cu-0.05Ga solders were obtained in the form of ingots from Nihon Superior (M) Sdn. Bhd. The raw materials were melted in the solder pot at 350°C for 1 hour by casting method. Stirring was then performed every 1 minute during the whole duration of 15 minutes to obtain homogenized solder alloys. A flat square-shaped copper plate with dimensions of 15 mm x 15 mm size and 1 mm thickness was used as a substrate. The substrates were cleaned using acid cleaning liquid that contain of 5g (35%) of hydrochloric acid with 95g of deionized water (1.75%) to remove surface oxides and contaminations.

2.2 Dipping Procedure

After the cleaning process, the dipping procedure was performed using a hot soldering machine. The process is chosen as it can save cost and reduce time consuming compared to the electroplating technique. Furthermore, the preparation of the solder will also be easier. Each substrate was hanged using a crocodile clip at the dipping machine. The dipping machine is equipped with a direct current (DC) motor with 12V power supply and 531 rpm speed. The substrate was first covered with flux before dipped in the solder pot containing molten bath for 20 seconds and blown at a pressure of 300 Mpa to get an even thickness. The thickness for each samples were measured at 50-70μm each. Then, the samples were cleaned again with acetone for 3 minutes using ultrasonic cleaner to remove the excessive flux.

2.3 Electromigration

After the dipping process, the samples were continued with the electromigration testing. The EM test for the dipping sample was performed by applying a direct current to both ends of sample with crocodile clips at the anode and cathode areas. Current density of 8.0x10⁴ A/cm² had been applied to the sample for 14 days at a room temperature by supplying a constant electric current to the solder joint. The testing parameters for dipping and electromigration testing are presented in Table 1.
### Table 1. Testing parameter for dipping and electromigration.

| Solder            | Sn-0.7Cu, Sn-0.7Cu-0.05Ga |
|-------------------|---------------------------|
| Substrate         | Copper                    |
| Dipping time      | 20s                       |
| Dipping temperature| 350°C-400°C               |
| Coating thickness | 50-60 µm                  |
| Current density   | $8.0 \times 10^4$ A/cm²   |
| Time for current stressing | 14days               |
| Current temperature| 30°C                     |

### 3 Result and Discussion

#### 3.1 Differential Scanning Calorimeter (DSC)

DSC analysis was performed to measure the melting characteristic and undercooling measurement of the solder alloy on the copper substrate. Fig. 1 shows the DSC curves of Sn-0.7Cu alloys, Sn-0.7Cu solder on Cu substrate, Sn-0.7Cu-0.05Ga and Sn-0.7Cu-0.05Ga solder on Cu substrate. From the below figure, the melting temperature of Sn-0.7Cu seems to be on the par with Ga addition. This is because the number of Ga addition is quite low compared to the previous research using 0.1% Ga [20]. Moreover, the melting temperature of both alloy on Cu substrate show the value has been decreased. This is because, the atom from the substrate had diffused from Cu to solder alloy. This resulted in a microstructure refining and reducing intermetallic compound thickness.

![DSC curve of the alloys.](image_url)
3.2 X-ray Diffraction (XRD)

XRD were performed on the bulk samples to identify all the existing phase using High Score software. From XRD curve, as the addition of Ga is only 0.05%, the secondary phases would not form. Ga element acts as a solid solution strengthening the elements that already diffused into the Sn atom.

![XRD pattern](image)

Fig. 2. XRD pattern of a) Sn-0.7Cu b) Sn-0.7Cu-0.05Ga.

3.3 Hardness Test

The hardness test of solder on copper substrate was tested with a Vickers hardness instrument. The load was tested at 1kg.f and dwelled in 20s. The test has revealed that the hardness value increases with the addition of Ga element compared to Sn-0.7Cu solder. The increase of the hardness value is likely due to the refinement of microstructure and uniform distribution of IMC phase in the solder alloy [21].

![Hardness value](image)

Fig. 3. Hardness value of the a) Sn-0.7Cu b) Sn-0.7Cu-0.05Ga.
3.4 Whiskers growth

Electrical current tests were performed to investigate the whisker growth. Fig. 4 shows the surface of Sn-0.7Cu and Sn-0.7Cu-0.05Ga after 8.0x10^4 A/cm^2 current stressing. The hillocks were observed on both solder alloy but the growth of hillock shows lower in length after Ga addition. This aligns with the previous study, where the growth of hillocks can release the compressive stress during electrical current stressing [5] [22]. Reduction in the hillock size is due to the small addition of Ga by altering the IMC growth during current stressing.

![Image of whiskers/hillock form on the solder](image1.png)

Fig. 4. The whiskers/hillock form on the solder a) Sn-0.7Cu and b) Sn-0.7Cu-0.05Ga after current stressing at 8.0x10^4 A/cm^2.

3.5 Microstructure of primary IMC and interfacial IMC

Fig. 5 shows the optical microscope image of Sn-0.7Cu and Sn-0.7Cu-0.05Ga solder. From the figure, the addition of Ga refines the grains structure and IMCs formation. Ga reduces the surface energy and allows for the smaller grains [20]. Also, Ga element will diffuse slowly and restricts the growth of the IMC particles and formation of secondary phases.

![Image of optical microscope image of primary IMC and ß-Sn of solder alloys](image2.png)

Fig. 5. Optical Microscope of primary IMC and ß-Sn of solder alloys a) Sn-0.7Cu and b) Sn-0.7Cu-0.05Ga solder.

Fig. 6 shows the IMCs formation before and after current stressing. IMCs layer is important for good bonding. It is essential to have good metallurgical contact between solder and substrate. In this study, the IMC formation is focused on the anode, middle and cathode sides in order to understand the effect of current stressing to the IMC and whiskers growth. From the figure, it can be seen that the IMC layer shows a refinement at the cathode side. This is mainly because the Ga element acts as a solid strengthening [20] that diffuses to the Sn atom during the electric current that flows from cathode to anode. The higher IMC thickness on the anode side is due to the fact that electron moves away from the cathode towards the anode [22]. Cu substrate was consumed along with the IMC growth. This resulted in the increment of Cu supply for the IMC growth at the anode. By electromigration, the Cu atoms has transported from the cathode to anode side which
improved the interfacial IMC growth at the anode. However, under electrical current stressing, the addition of Ga to the solder inhibits the diffusion of Cu and Sn to the anode which furthermore reduces whiskers formation.

![Image](image_url)

**Fig. 6.** Interfacial IMCs of Sn-0.7Cu-0.05Ga before and after electromigration.

### 4 Conclusion

As a summary, this paper investigates the relation of electrical current testing on the tin whiskers formation. Moreover, the results of addition of Ga as the microalloying to the Sn-0.7Cu were systematically presented in this paper. Other results are summarised as below:

- Thermal properties of Sn-0.7Cu has been improved with the addition Ga elements.
- XRD phase analysis shows the present of Cu₆Sn₅ element in the Sn-0.7Cu and Sn-0.7Cu-0.05Ga solder alloy
- The initial IMC has scallop-type morphology and Cu₆Sn₅ forms and grows with or without current.
- Whiskers length have increased with the Ga addition.
- The hardness value increased with the Ga addition which refined the grains and IMC formation.

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