Intermetallic Growth Retardation with the Addition of Graphene in the Sn-3.5Ag Lead-free Solder

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Abstract. In this study, the effect of 0.07 wt.% graphene nanosheets (GNSs) on the thermal, microstructure and intermetallic compounds (IMC) growth kinetics were investigated. Experimental results showed that addition of GNSs to the Sn-3.5Ag solder alloy slightly increased the melting temperature. Scanning electron microscope (SEM) micrograph revealed that with the addition of GNSs has transformed the morphologies of the interfacial IMC from scalloped to more planar-shaped after isothermal aging for 500 hours. Growth kinetics calculations show that the k value was reduced from 9.08 x 10^{-14} \text{ cm}^2/\text{s} to 5.73 x 10^{-14} \text{ cm}^2/\text{s} with the addition of graphene. Thereby, it indicates that the addition of GNSs suppressed the growth of the IMC layers hence retarded the IMC’s growth.

1. Introduction
In recent times, many lead-free solders have been developed in the electronic packaging industry as a replacements for the conventional Sn-Pb solder even though the Sn-Pb solder has been widely used due to their lower melting temperatures and good wetting behavior. Due to the harmful effect to human health and legislative pressures, the electronic industry is refocusing toward implementation of lead-free solders. Among them, the Sn-Ag alloy systems with or without the additions of other alloying elements is considered as one of the best promising candidate because of its mechanical and electrical properties [1-2].

Nevertheless, one of the main problem related to the use of Sn-3.5Ag is an excessive reaction between the solder and substrate which results to large brittle formation of intermetallic compounds (IMC) [3]. IMC is a layer that generated by chemical reaction between solder alloy and substrate during the soldering process which can grow via diffusion in the solid state. For the Sn-Ag/Cu couple, the interfacial IMC layer consists of Cu6Sn5 and Cu3Sn binary compounds and these layer were generated during the soldering process and grew in the high temperature environment [4]. Many studies have been done to further improve the solder properties in order to reduce the IMC growth by adding extra element such as In, Bi, and Zn into the solder alloys [5-8]. Recently, nano-composite solders have been developed due to rapidly changes in technologies and moving towards miniaturized of consumer electronic products including the size of electronic components. The reinforcements of nano-particles to the solder alloys could result in self-organized dispersive systems, which contribute to the heterogeneous nucleation, thus causing the stress in the solder joints to be dispensing uniformly [9-10]. Among all the micrometer and nanometer sized particles as a new reinforcement, graphene has attracted the attention of researchers due to its excellent mechanical, electrical and thermal properties. Few studies [11-13] reported that addition GNSs into the pure solder has showed improvement of mechanical properties. Thus, this present work investigated the effects addition of 0.07 wt.% graphene

nanosheets (GNSs) into Sn-3.5Ag solder on thermal and microstructure formation of IMC. In view of this information, the isothermal aging were done to study the reactions between the solders and Cu substrate to understand the formation and growth mechanism of IMC.

2. Methodology.

2.1. DSC measurement for melting point
Melting characteristics of the Sn-3.5Ag and Sn-3.5Ag-0.07GNSs solders were investigated using differential scanning calorimeter (Jade DSC Perkin-Elmer). The solder samples were heated to 250 °C at heating rate of 10 °C/min. The entire scanning was carried out under inert nitrogen atmosphere.

2.2. Interfacial study of the IMC
Composite solder was prepared by powder metallurgy route method by mixing 0.07 wt.% of graphene nanosheets (GNSs) into Sn-3.5 wt.%Ag solder. The mixtures were blended mechanically for 2 hours for Sn-3.5Ag and 10 hours for Sn-3.5Ag-0.07GNSs with 200 rpm speed to achieve uniform distribution. A similar mixing method was used by other researchers [14]. The range diameter of the GNSs used is 0.5–2.0µm and 25 nm of thickness. Then the mixtures were compacted into disc shape with a diameter of 12 mm at 14 MPa and sintered at 150 °C for 2 hours in the argon gas atmosphere. For the study of interfacial reactions, the Sn-3.5Ag and Sn-3.5Ag-0.07GNSs solders were placed on the Cu substrate and molten at 250 °C for one minute. The samples were isothermally aged at 150 °C for 100, 200, 300, 400 and 500 hours. The solder joint was mounted in epoxy, cross-sectioned, polished with silicon carbide (SiC) papers until 2000 grit and final polishing was done with 1.0 and 0.3 µm silica powders, and etched for 1 seconds to reveal the intermetallic microstructure. The Cu/solder interface was then analysed under Scanning Electron Microscope (SEM) and the average thickness of the intermetallic was calculated by using imageJ software.

3. Results and Discussions.

3.1. Thermal behavior
Differential scanning calorimetry (DSC) analysis was done to investigate the fundamental thermal effect during heating process of these two solders. Figure 1 illustrate the DSC curves of Sn-3.5Ag and Sn-3.5Ag-0.07GNSs through heating process. During the endothermal process, only one eutectic peak was observed for Sn-3.5Ag solder, and the onset and peak temperatures appeared at 224.83 °C and 228.92 °C, respectively. With the addition of GNSs nanoparticles, the onset and peak temperatures slightly changed towards the right. The onset and peak temperatures of the Sn-3.5Ag-0.07GNSs increased to 225.03 °C and 230.20 °C, respectively. These results show that the addition of GNSs has a little effect on the $T_{\text{onset}}$ and $T_{\text{peak}}$ which is <1.3 °C. The reason could be that the reinforcing nano-sized of GNSs particles into Sn-3.5Ag solder changed the surface instability and variation in physical properties of grain boundary/interfacial characteristics. Such particles may serve as restrained sites for the solidification process of IMCs as well as β-Sn grains. The literature [15] shows that the addition of little amount of graphene oxide nanosheets has slightly increased the melting point of Sn-55Sb-1Ag nanocomposite solder. So, its influence on the melting point of composite solder can be ignored because of its low GNSs content as reported by some researchers [12].
3.2. Morphology of the Intermetallic.
The SEM micrographs of Sn-3.5Ag/Cu and Sn-3.5Ag-0.07GNSs/Cu are shown in figures 2 to 5. Figures 2a and 2b present the solder joint after reflowed for 1 minute at 250 °C, in which the interfacial Cu₆Sn₅ IMC layer is very thin (average about 2.1 ~ 2.4 µm), scallop-like shaped and appeared in light gray layer. Based on previous study [16], a single layer of Cu₆Sn₅ intermetallic compound layer was also observed at the solder/Cu interface during the soldering process of Sn-Pb and Sn-Zn solders.

![Figure 1. DSC result during heating for Sn-3.5Ag and Sn-3.5Ag-0.07GNSs solders.](image)

**Figure 1.** DSC result during heating for Sn-3.5Ag and Sn-3.5Ag-0.07GNSs solders.

![Figure 2. IMC formation for as-soldered for 1 min at 250 °C for (a) Sn-3.5Ag/Cu and (b) Sn-3.5Ag-0.07GNSs/Cu solder joints.](image)

**Figure 2.** IMC formation for as-soldered for 1 min at 250 °C for (a) Sn-3.5Ag/Cu and (b) Sn-3.5Ag-0.07GNSs/Cu solder joints.

![Figure 3. IMC formation for (a) Sn-3.5Ag/Cu and (b) Sn-3.5Ag-0.07GNSs/Cu solder joints after aged for 100 hours.](image)

**Figure 3.** IMC formation for (a) Sn-3.5Ag/Cu and (b) Sn-3.5Ag-0.07GNSs/Cu solder joints after aged for 100 hours.
The IMC layers become thicker (3.5 – 6.5 µm) and turn to more planar-like shape when aging time increasing (figures 3-5). When samples were aged for 300 hours, the Cu$_3$Sn layer was observed at the interface between Cu$_6$Sn$_5$ intermetallic compound and Cu substrate for the Sn-3.5Ag-0.07GNSs solder joint (figure 4b). Since the Cu$_6$Sn$_5$ intermetallic has lower activation energy compared to Cu$_3$Sn, so it was the first phase that formed at the substrate/solder interface while Cu$_3$Sn layer required more time to generate. As the aging time prolonged until 500 hours (figure 5) the Cu$_3$Sn layer was appeared for both Sn-3.5Ag and Sn-3.5Ag-0.07GNSs solder joints. The solder joints with the addition of graphene showed decreasing in intermetallic thickness formation at the interface compared to the Sn-3.5Ag solder joints. Some voids were also appeared in the solder interfacial for Sn-3.5Ag-0.07GNSs/Cu solder joints which may be due to the present of graphene nanosheets in the solder matrix.

![Figure 4](image-url). IMC formation for (a) Sn-3.5Ag/Cu and (b) Sn-3.5Ag-0.07GNSs/Cu solder joints after aged for 300 hours.

![Figure 5](image-url). IMC formation for (a) Sn-3.5Ag/Cu and (b) Sn-3.5Ag-0.07GNSs/Cu solder joints after aged for 500 hours.

![Figure 6](image-url). The $d - d_0$ of the IMC layer thickness with respect to different isothermal aging time.
The average values of thickness during aging, $d$, was plotted against the square root of aging time, $t$, as shown in figure 6. The expression for diffusion controlled mechanism is given by:

$$d - d_0 = k^{1/2} t^{1/2}$$  \hspace{1cm} (1)

where $d_0$ is the initial thickness of IMC layer and $k$ is growth rate constant. Using this relation, the value of $k$ was calculated to be higher for Sn-3.5Ag which is $9.08 \times 10^{-14}$ cm$^2$/s compared to $5.73 \times 10^{-14}$ cm$^2$/s for Sn-3.5Ag-0.07GNSs solder. This indicates that the reinforcement of GNSs into Sn-3.5Ag solder has suppress the growth rate of IMC formation between the solder and the substrate.

4. Conclusion

The melting temperature and interfacial microstructure of Sn-3.5Ag and Sn-3.5Ag-0.07GNSs solders were investigated. Addition of 0.07 wt.\% of GNSs into Sn-3.5Ag solder slightly increased the melting temperature. A scallop layer of IMC was generated at the interface during the soldering. The morphology of IMC changed from scallop-like to irregular shape IMC during isothermal aging till 500 hours for both solder joints. The Sn-3.5Ag-0.07GNSs solder joints in general exhibit lower growth rate as compared to Sn-3.5Ag solder joints. It indicated that GNSs can effectively retard the IMC’s layer growth.

Acknowledgement

This study is financially supported by The Minister of Higher Education (MOHE) for the Grant 600-RMS/FRGS 5/3 (104/2015). Authors also thank Universiti Teknologi MARA and UniMAP for facilities.

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