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Review Article

Interfacial Reaction of Sn-Ag-Cu Lead-Free Solder Alloy on Cu: A Review

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This paper reviews the function and importance of Sn-Ag-Cu solder alloys in electronics industry and the interfacial reaction of Sn-Ag-Cu/Cu solder joint at various solder forms and solder reflow conditions. The Sn-Ag-Cu solder alloys are examined in bulk and in thin film. It then examines the effect of soldering conditions to the formation of intermetallic compounds such as Cu substrate selection, structural phases, morphology evolution, the growth kinetics, temperature and time is also discussed. Sn-Ag-Cu lead-free solder alloys are the most promising candidate for the replacement of Sn-Pb solders in modern microelectronic technology. Sn-Ag-Cu solders could possibly be considered and adapted in miniaturization technologies. Therefore, this paper should be of great interest to a large selection of electronics interconnect materials, reliability, processes, and assembly community.

1. Introduction

Among various alloy systems that are considered as lead-free solder candidates, Sn-Ag-Cu alloys have been recognized as the most promising because of their relatively low melting temperature (compared with the Sn-Ag binary eutectic lead-free solder), superior mechanical properties, and good compatibility with other components [1–3]. Sn-Ag-Cu alloys are widely used as lead-free solutions for ball-grid-array (BGA) interconnection in the microelectronic packaging industry as solder balls and pastes [4].

Among bumping materials, a family of solder alloys based on the ternary Sn-Ag-Cu eutectic (217°C) composition has the most potential for broad use in the industry [5]. The eutectic composition is favourable to be chosen because it behaves as an independent homogenous phase and has a unique metallographic structure and a distinct melting point [6]. Sn-Ag-Cu solders can promote enhanced joint strength as well as creep and thermal fatigue resistance and can permit increased operating temperatures for the fabrication of advanced electronic systems and devices [7, 8]. The International Printed Circuit Association has suggested that 96.5Sn-3.0Ag-0.5Cu (SAC305) and Sn-3.9Ag-0.6Cu (two near-eutectic alloys) will be the most widely used alloys in the future [7]. This prediction is attributed to their good mechanical properties, acceptable wetting properties, and suitable melting points [2, 3, 9–11].

Lead-free solder joints have been reported to have fine and stable microstructures because of the formation of small-dispersed particles. Thus, these joints have higher shear strengths [12, 13]. Sn-Ag-Cu solders require a higher reflow temperature because of its higher melting point. For instance, the melting point of Sn-3.8Ag-0.7Cu is 219°C, and that of SAC305 is 217°C. The high melting temperature not only requires a new reflow profile, but also increases the component stability concerns that accompany a higher temperature. Several components may not survive at a high reflow temperature.

2. Lead-Free Solder and Its Applications

Soldering is a well-recognized metallurgical joining method to bond solder to a base material (usually metal) at a melting point below 425°C [14]. Let us take Figure 1 as an example. During the soldering process, the SAC305 solder wire (Figure 1(a)) melts and gets into contact with Cu substrate base metal (Figure 1(b)). Moreover, the Sn in the molten solder

Figure 1: Appearance change of (a) a coiled SAC305 solder wire into (b) a solid SAC305 solder on the Cu substrate during solder reflowing.

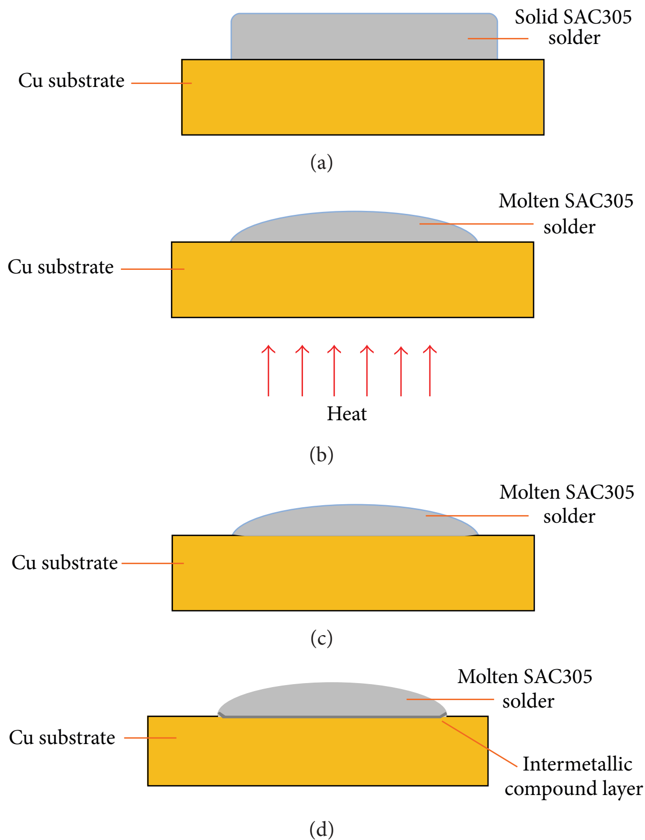

Figure 2: Solder wetting process: (a) SAC305 solder on the Cu substrate, (b) liquid solder spreading over the Cu substrate during soldering, (c) Cu diffuse in the liquid solder, and (d) Cu reacting with the liquid solder to form an intermetallic compound layer.

reacts with Cu to form intermetallic compound (IMC) on the interface. It is this IMC layer that bonds the solder and Cu together [15–20].

Generally, the soldering process is portrayed in Figure 2. The soldering process can be divided into three stages [21]:

(a) spreading;

(b) base metal dissolution;

(c) formation of an IMC layer.

The Cu substrate did not melt or change its microstructure during soldering. The liquid phase then transformed to various solid phases when the joints were cooled down. The different kinds and relative amounts of the solid phases formed during solidification are important for solder joint properties.

Solders are usually low melting point alloys because soldering is conducted when the solders are completely molten [22]. The products are used at their solid phases at relatively high operation temperatures. Hence, diffusivity is an important property for most solders. In addition, good wetting is required for good solders; thus, interfacial reactions with substrates are usually important not only at the liquid/solid contacts, but also at the solid/solid contacts at high operation temperatures [22].

The solder joint strength is controlled by the land pattern design and a good metallurgical bond between the component and the board. A reliable solder connection must have a solderable surface to form a good metallurgical bond between the solder and the components being joined. Interfacial reactions at the solder joints are key factors in the fabrication of electronic products.

3. IMC of Sn-Ag-Cu Solders with Cu Substrate

In electronic products, all common base materials, coatings, and metallizations, such as Cu, Ni, Ag, Ag-Pd, and Au, form IMCs with Sn. Therefore, chemical reactions occur between solders and conductor metals during soldering (i.e., component metallizations, board surface finishes, and underlying conductors), and IMCs nucleate and grow at the solder/conductor interfaces.

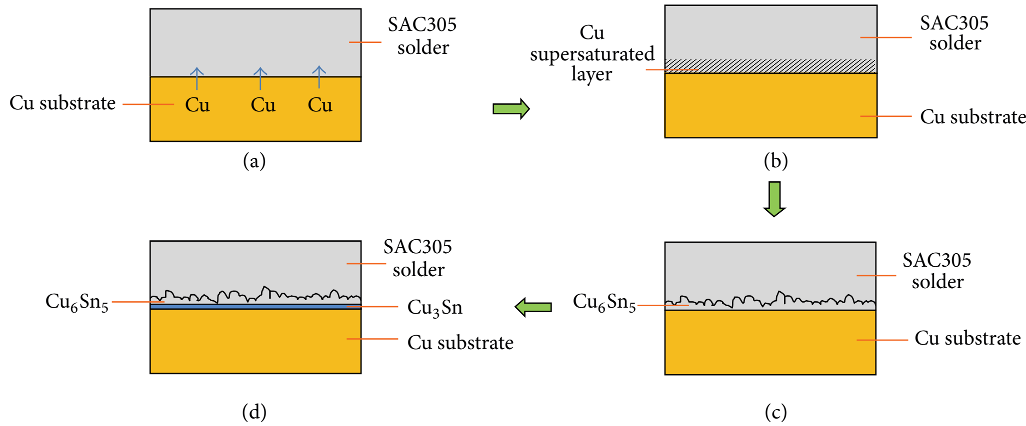

Figure 3: Scheme of the interfacial reaction of SAC305/Cu during solder reflow: (a) dissolution of the Cu substrate, (b) supersaturation of the molten solder layer with Cu, (c) formation of the scallop-type Cu_6Sn_5 at the interface, and (d) Cu_3Sn emerges between Cu_6Sn_5/Cu with prolonged soldering.

The presence of IMCs between solders and conductor metals is desirable because it results in good metallurgical bonding. A thin, continuous, and uniform IMC layer is an essential requirement for good bonding. Without IMCs, the solder/conductor joint is weak because no metallurgical interaction occurs in the bonding, which is disastrous to electronic packaging. However, a thick IMC layer at the solder/conductor metal interface may degrade the reliability of the solder joints because of their inherent brittle nature and their tendency to generate structural defects caused by mismatches of the physical properties (such as elastic modulus and coefficient of thermal expansion) [23]. A thick IMC layer should be avoided during the process. Thus, knowledge of the solder/conductor metal interactions and phase evolution in the solder interconnections is important to understand the reliability of solder interconnections from a metallurgical viewpoint and to optimize the soldering process [17].

The intermetallic reaction layers are formed in three consecutive stages [17]:

(a) dissolution;

(b) chemical reaction;

(c) solidification.

During the soldering of the Sn-Ag-Cu solder on the Cu substrate, the Cu starts to dissolve instantaneously to the molten solder after the flux removed the oxides and permitted metallurgical contact between the solder and contacted Cu. The initial rate of dissolution is very high. The dissolution is a nonequilibrium process, and a very high concentration of Cu could be locally found in the Cu/liquid interface. After a short duration of time, the layer of molten solder adjacent to the contacted Cu becomes supersaturated with the dissolved Cu throughout the interface.

From a thermodynamics viewpoint, the solid IMC starts to form in the layer of the solder adjacent to the contacted metal at the local equilibrium solubility. Cu_6Sn_5 crystallites are formed because a large driving force for the chemical reaction between Cu and Sn atoms exists at the metastable composition. Scallop-type Cu_6Sn_5 first formed at the Sn/Cu interface during soldering, and its rate of formation is very fast. Cu_6Sn_5 was formed by the dissolution of Cu, followed by a chemical reaction. If contact with the molten solder is long enough, Cu_3Sn formed between Cu_6Sn_5 and Cu. Cu_3Sn was formed by diffusion and by reaction type growth [24].

Figure 3 briefly illustrates the interfacial reaction of SAC305/Cu during solder reflow. When heat is applied, the solid SAC305 solder melts, and the contacted Cu substrate starts to dissolve to the molten SAC305 solder (Figure 3(a)). The layer of molten SAC305 solder near the SAC305/Cu interface becomes supersaturated with the dissolved Cu (Figure 3(b)). The solid IMC begins to form at the interfacial zone. Cu_6Sn_5 with a scallop structure was first formed (Figure 3(c)), followed by thin layer-like Cu_3Sn (Figure 3(d)).

4. Structural Phases of IMCs in Sn-Ag-Cu/Cu

Cu is the most frequently used conductor metal, and it is utilized in contact with solders because of its good solderability characteristic and excellent thermal conductivity performance [25]. Liu et al. [26] investigated the interfacial reactions between a SAC305 solder paste and a polycrystalline Cu substrate at 250°C and 300°C from 30 s to 1800 s. They found that some nanosized Ag_3Sn particles were adsorbed on the SAC305/Cu interface after soldering. The authors explained that Ag atoms first reacted with Sn to form an Ag_3Sn phase in the liquid solder. During solidification, the Ag_3Sn phase precipitated near the IMCs and was prone to be "captured" by the IMCs. Moreover, Wang et al. [27] performed X-ray diffraction (XRD) analysis on interfacial SAC305/Cu to examine the phase structure of IMC during soldering at 260°C for 20 s. The XRD pattern indicates that the crystal structure of IMCs for SAC305/Cu is Cu_6Sn_5. However, no Ag_3Sn phase was detected in this case.

The XRD patterns of SAC305 in various solder forms are shown in Figure 4. The overall intensity of the SAC305 solder wire was much lower than that of the as-deposited

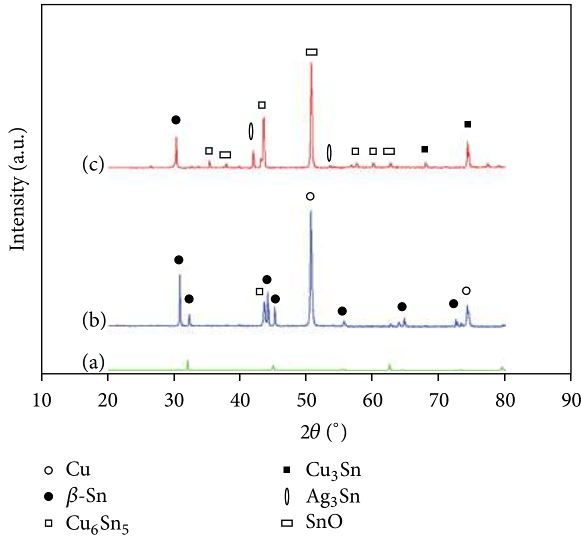

Figure 4: XRD patterns from the top surface of (a) SAC305 solder wire, (b) as-deposited SAC305 thin film, and (c) as-reflowed SAC305/Cu.

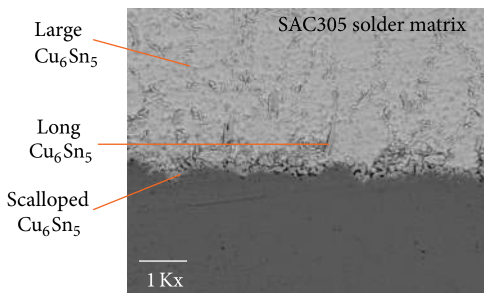

Figure 5: FESEM image of SAC305 solder joints with the Cu substrate.

SAC305 thin film and of the as-reflowed SAC305/Cu. The as-deposited SAC305 thin film exhibited β-Sn, $\acute{\eta}$-Cu_6Sn_5, and Ag_3Sn reflections. Heating the SAC305 solder wire did not result in phase changes, except in its relative intensity. The peaks of Cu_6Sn_5 and Ag_3Sn were too low to be seen in the XRD pattern of the SAC305 solder wire (Figure 4(a)), which had lower intensity than that of the as-deposited SAC305 thin film (Figure 4(b)). After solder reflow at 230°C, most β-Sn phases diminished (Figure 4(c)). By contrast, the diffraction peaks of $\acute{\eta}$-Cu_6Sn_5 and Ag_3Sn became more evident. New phases of IMCs formed and were confirmed as η-Cu_6Sn_5, ε-Cu_3Sn, and SnO.

5. Microstructure Evolution of IMCs in Sn-Ag-Cu/Cu

Kar et al. [28] evaluated the microstructure of a transition joint consisting of an Sn-Ag-Cu solder alloy and a Cu substrate in a reflowed condition at 230°C for 120 s. They confirmed the presence of Cu_6Sn_5, Cu_3Sn, and Ag_3Sn intermetallic phases at the interfacial reaction layer (IRL). The presence of Ag in the IRL was minimal and did not take part in the formation of IMCs at the interface. Gao et al. [29] assumed that a significant quantity of Ag was entangled with Sn to form Ag_3Sn within the solder alloy. Thus, the extent of diffusion of Sn towards the IRL was reduced.

One of the characteristics of IMC is the formation of a scallop-type morphology. Scallop-type Cu_6Sn_5 IMCs were formed at SAC305/Cu interfaces, whereas the solder was in the molten state during the reflow at 270°C for 120 s [30]. This result also corresponds to the study done by Kim et al. [1] on the effect of IMC on a SAC305 solder alloy (in the form of pastes and balls) with a Cu substrate joint after reflow treatment at 260°C. Yoon and Jung [31] also investigated the interfacial reaction of Cu/Sn-3.5Ag-0.7Cu/Cu sandwich solder joints. Typical scallop-type Cu_6Sn_5 IMC layers were formed at both Sn-3.5Ag-0.7Cu/Cu interfaces after reflow. The layers had a composition of approximately 54.8 at.% Cu and 45.2 at.% Sn.

Figure 5 displays the cross-sectional FESEM micrograph of the as-reflowed SAC305/Cu sample. The reaction layer on the Cu substrate is the scallop Cu_6Sn_5 phase, which was formed during the reflow treatment. Long Cu_6Sn_5 IMCs were observed at the top of the interfacial Cu_6Sn_5 scallops, and the growth is attributed to the Cu flux from the Cu substrate to the scallops [32]. However, relatively large Cu_6Sn_5 IMCs were formed in the solder matrix because of the dissolution of the Cu pad. Some Cu pads were dissolved in the molten SAC305 solder during reflow, and the dissolved Cu was precipitated as large Cu_6Sn_5 IMCs in the solder matrix. In other words, the solidification of a eutectic SAC305 solder produced a mixture of β-Sn matrix, fine Ag_3Sn, and Cu_6Sn_5 IMC particles.

Moreover, Ag_3Sn IMC was uniformly dispersed in the solder after reflow [33]. A microstructural analysis on Sn-Ag-Cu solder alloys with different Ag contents was performed to understand the microstructure details and to evaluate the formation of intermetallic compounds. Elongated plates of the ε-Ag_3Sn phase were observed in the eutectic matrix of Sn-1.0Ag-0.5Cu (SAC105), Sn-2.0Ag-0.5Cu (SAC205), and SAC305 solder alloys. On the other hand, large ε-Ag_3Sn intermetallics plates and elongated plates of the ε-Ag_3Sn phase were clearly seen in the Sn-4.0Ag-0.5Cu (SAC405) solder alloy. Figure 6 illustrates the morphologies of Ag_3Sn IMCs in the solder matrix, which can be changed by varying the Ag content. Ag_3Sn IMCs of elongated plate-like structure exist when the Ag content is between 1.0 and 3.0 wt% (Figure 6(a)). A higher Ag composition of 4.0 wt% results in the formation of large Ag_3Sn IMCs, as in Figure 6(b).

The overall reliability can be greatly affected by the amount and size of ε-Ag_3Sn IMCs in the microstructure. Large ε-Ag_3Sn IMCs are generally believed to be detrimental in both crack initiation and propagation, and numerous studies have attributed the failure of SAC305 solders to large plate-like ε-Ag_3Sn IMCs under impact and thermal cycling stimuli [1, 34, 35]. In addition, the formation of large plate-like ε-Ag_3Sn IMCs causes solid dissolution and precipitation hardening, which in turn decreases the matrix strength [36, 37].

Figure 7 shows the interfacial reaction of the SAC305 thin film deposited by the thermal evaporation technique. The thin film was subsequently reflowed at 230°C for 30 s. The

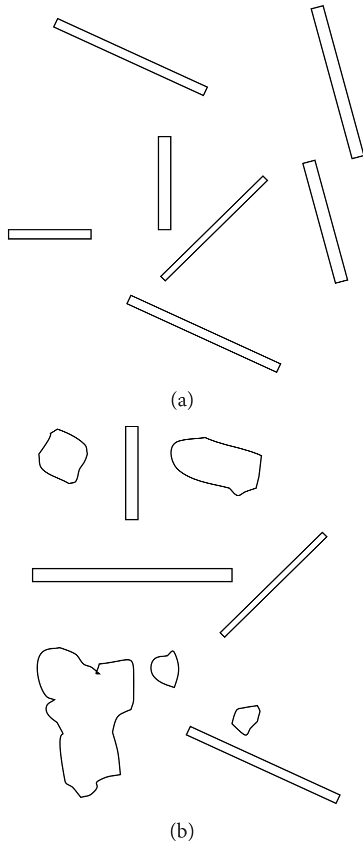

Figure 6: Morphologies of Ag_3Sn compound at varying Ag concentrations with (a) 1.0 Ag to 3.0 Ag alloying and (b) 4.0 Ag alloying.

top white layer is the SAC305 solid layer, which comprised loose SAC305 particles that were physically adsorbed on the Cu substrate (Figure 7(a)). After solder reflow, interfacial reaction occurred. As shown in Figure 7(b), two layers of IMCs were formed. The top region is Cu_6Sn_5, and the layer beneath is Cu_3Sn. Cu_6Sn_5 was thick and irregular in thickness, whereas Cu_3Sn was very thin and had a more uniform thickness and a layer-like morphology. However, the thin layer followed the topography of the adjacent Cu_6Sn_5 phase layer to a particular extent. No spalling or flaking of the IMCs was observed, which indicates that the Sn concentration in the thin film was low. The thin film SAC305 solder completely reacted with excess Cu substrate to form Cu_6Sn_5 during reflow. The Cu_3Sn intermetallic layer consistently increased with increasing temperature, whereas Cu_6Sn_5 gradually decreased with increasing reflow temperatures.

6. Formation and Growth Kinetics of Interfacial IMCs

The formation of scallop Cu_6Sn_5 has been observed in wetting reactions between eutectic Sn-Pb and Cu [38–40], eutectic Sn-Ag and Cu [39], and eutectic Sn-Bi and Cu [39]. The scallop is a common growth mode, which grows bigger but fewer with time. This behavior indicates that a nonconservative ripening reaction occurs among scallop-type grains. Furthermore, the scallop-type morphology is stable as long as unreacted Cu is present.

In a Cu-Sn system, Cu_6Sn_5 and Cu_3Sn IMCs form at solder/substrate interfaces [1, 39, 41–47]. The actual formation sequence of these phases is determined by local thermodynamic conditions at the Cu/Sn interface. The Cu_6Sn_5 phase precipitates during the earliest stages of solder/substrate interactions, which correspond to a higher driving force for precipitation than that of the Cu_3Sn phase [48, 49]. The Cu_6Sn_5 phase has been experimentally confirmed to precipitate in a random fashion along the solder/substrate interface.

The formation and growth of interfacial Cu-Sn IMCs is illustrated in Figure 8. During the initial stage (Figure 8(a)), individual Cu_6Sn_5 grains appear at random locations along the solid/liquid interface within a few milliseconds. After the Cu_6Sn_5 grains appear, they began to spread along the interface without much growth perpendicular to the solder/substrate interface until they encounter other spreading grains, which resulted in the formation of a relatively uniform IMC layer of Cu_6Sn_5 (Figure 8(b)).

After the initial formation of the IMC layer, its thickness grows at the expense of the underlying substrate. The individual grains acquire a scallop-like morphology [50] that continues to grow perpendicularly to the interface (Figure 8(c)). The ripening process contributes to the formation of the scallop structure of IMCs, which result in the coarsening of the scallops as its number is decreasing (Figure 8(d)). This reaction is driven by the Gibbs-Thomson effect in the ripening process. Thus, smaller IMC grains are dissolved in the liquid solder, and the growth of neighboring grains is further promoted [39, 51, 52].

After the precipitation of the Cu_6Sn_5 phase, the precipitation of the Cu_3Sn phase at the Cu_6Sn_5/substrate interface becomes thermodynamically possible. This phenomenon is usually observed during the later stages of the soldering reactions. The thickness of Cu_3Sn is expected to be much smaller than that of Cu_6Sn_5 because Cu_3Sn was grown by solid state diffusion.

The evolution of Cu-Sn IMCs for Sn-Ag-Cu/Cu couples is based on the continuous growth of Cu_6Sn_5 via soldering and on the formation and growth of Cu_3Sn between Cu_6Sn_5 and Cu. The formation of Cu_3Sn is governed by the phase stability according to the following reaction [29]:

$$Cu_6Sn_5 + 9Cu \longrightarrow 5Cu_3Sn \quad (1)$$

Vianco [53] found the formation of Cu_6Sn_5 and Cu_3Sn at the interface between Cu and 95.5Sn-3.9Ag-0.6Cu. The author concluded that Cu_6Sn_5 layer was formed during soldering and Cu_3Sn forms during solid state ageing between Cu_6Sn_5 and Cu substrate. The layer growth is diffusion limited and sensitive to the CU concentration in the solder.

The remaining amount of components, which are involved in the interfacial reaction, takes part in phase evolution after the formation of the first phase. In the Sn-Pb/Cu system, the Cu_6Sn_5 layer that first formed transforms into Cu_3Sn if the solder volume is very small compared with

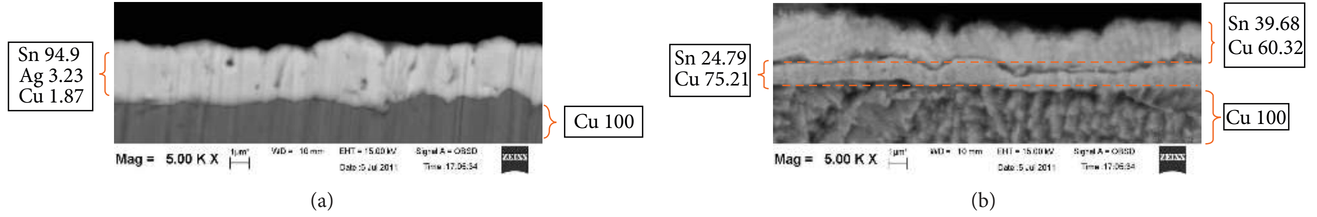

Figure 7: FESEM micrographs of the cross-sectional surface of (a) as-deposited SAC305 thin film and (b) as-reflowed SAC305/Cu at 230°C for 30 s.

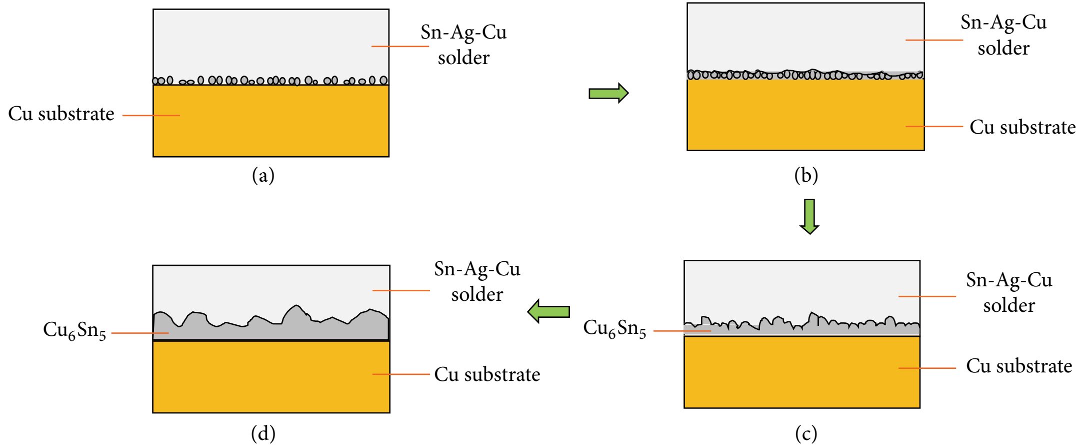

Figure 8: Schematic diagram of the growth mechanism of Cu_6Sn_5 at the Sn-Ag-Cu/Cu interface: (a) individual Cu_6Sn_5 grains at the interface, (b) Cu_6Sn_5 growth along the interface, (c) the ripening process resulted in scallop Cu_6Sn_5, and (d) coarsening of scallop Cu_6Sn_5.

that of Cu [54, 55]. Conversely, the Cu_3Sn converts back to Cu_6Sn_5 if the thin film is Cu [56]. Cu_3Sn could dissolve itself to produce Cu_6Sn_5, and it also could react with Sn atoms to form Cu_6Sn_5 [3, 57]. The transformation equations from Cu_3Sn to Cu_6Sn_5 are shown as follows:

$$5Cu_3Sn \longrightarrow 9Cu + Cu_6Sn_5 \quad (2)$$

$$2Cu_3Sn + 3Sn \longrightarrow Cu_6Sn_5 \quad (3)$$

During cooling, the outer layer of Cu_3Sn that is in contact with the molten solder transforms back to Cu_6Sn_5 by the peritectic reaction

$$L + Cu_3Sn \longrightarrow Cu_6Sn_5 \quad (4)$$

Many models exist to forecast the first phase formation of solid state interfacial reactions in thin films. The kinetics of growth of each layer can be diffusion or interfacial reaction controlled. The largest product of the Gibbs free energy change and the rate of growth determines the formation of the first phase. In other words, the phase that has the largest flux of interdiffusion becomes the first phase that is formed.

The difference in IMC growth rates is attributed to various growth kinetics [58]. Diffusion rates control the IMC growth rate, whereas different solder/IMC interface energies control the coarsening of the IMC grains and nucleation kinetics. The IMC growth in solder joints is considered to be an ordinary diffusion growth and should be controlled by interdiffusion of elements of the substrates and of the solder. Interfacial IMCs layers continue to grow even at room temperature after the solder joints have completed solidification because of its low activation energy [59, 60].

If the IMC layer growth is a diffusion dominant process, the isothermal growth of the IMC layer should follow the square root time law. The thickness (d) of an IMC layer is directly observed with FESEM together with the help of a image processing system and can be expressed by parabolic equation [61]

$$d = d_0 + \sqrt{kt}, \quad (5)$$

where d_0 is the initial thickness (cm), t is the aging time (s), and k is the growth rate constant which is strongly related to the diffusion coefficient of atomic elements of the IMC (cm^2/s) and can be obtained from the linear regression line.

Rewrite (5) for experimental and plotting purposes as

$$d - d_0 = k^{1/2} t^{1/2}. \quad (6)$$

The value of k for a particular temperature can be obtained from the slope of the linear regression of the average measured intermetallic thickness ($d - d_0$) versus $t^{1/2}$ plot.

Meanwhile, the activation energies for the intermetallic growth can be calculated using the Arrhenius relationship [43]:

$$k = k_o \exp\left(-\frac{Q}{RT}\right). \quad (7)$$

Rewrite (7) for plotting as

$$\ln k = \ln k_o - \frac{Q}{RT}, \quad (8)$$

where k_o is the layer-growth constant (cm^2/s), Q is the activation energy for layer growth (kJ/mol), R is the ideal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The Q for layer growth will be obtained from the slope of the $\ln k$ versus $1/T$ plot multiplied by R.

7. Effects of Reflow Temperature and Time on Interfacial IMCs

The thicknesses of the IMC layers are measured at multiple selected areas and then divided by the number of selected points to obtain the average value, as illustrated in Figure 9. The thickness of the IMC layers formed at the SAC305/Cu interface increases with increasing soldering temperature and time. Cu-Sn IMCs were formed at the interface of Sn-0.3Ag-0.7Cu and the Cu substrate by dip soldering in various soldering temperature and time [62]. Either Cu_3Sn or Cu_6Sn_5 intermetallic phase was found at the interfacial zone depending on the soldering condition. The authors concluded that the increase in intermetallic layer thickness in both cases is attributed to the diffusion growth of these intermetallic phases during the soldering process.

Additionally, Yu et al. [61] studied the formation and growth of IMC layer at the interface between Sn-3.5Ag lead-free solder and the Cu substrate during soldering and aging. The soldering was conducted at 250°C using dipping method. A continuous IMC layer was formed in a short time, and the dissolution of the IMC played an important role on the IMC growth. With the increasing of soldering time, both the growth rate and dissolution rate decreased. During aging at 70, 125, and 170°C up to 1000 h, the initial scallop morphology of the IMC layer changed to that of a more planar type.

The increase in IMC thickness that resulted from increasing soldering time has also been reported by Yu and Wang [3]. The authors soldered Sn-3.5Ag, Sn-3.5Ag-0.7Cu, Sn-3.5Ag-1.7Cu, and Sn-0.5Ag-4.0Cu lead-free solder alloys with a Cu substrate at 250°C. The growth of the IMC layers is fast at a short soldering time. The thickness of the IMC layer gradually increases with increasing soldering time. However, the increasing rate of IMC thickness slows down when the soldering time exceeds 60 s. Thus, the authors concluded that the formation of IMC is initially controlled by reaction diffusion and by a high growth rate. After a specific thickness is reached, the growth is controlled by grain boundary diffusion mechanism. Hence, the growth of the IMC layer becomes slow, as shown in Figure 10.

The authors also concluded that Sn-0.5Ag-4.0Cu had the thinnest IMC layer when the soldering time is shorter than 90 s. After soldering for 600 s, the order of IMC thickness at the solder joints is Sn-3.5Ag < Sn-3.5Ag-0.7Cu < Sn-3.5Ag-1.7Cu < Sn-0.5Ag-4.0Cu. Thus, the IMC thickness increased with increasing Cu content in the solder alloy. Moreover, the IMCs layer thickness quickly increased with increasing soldering time because of the precipitation effect of the

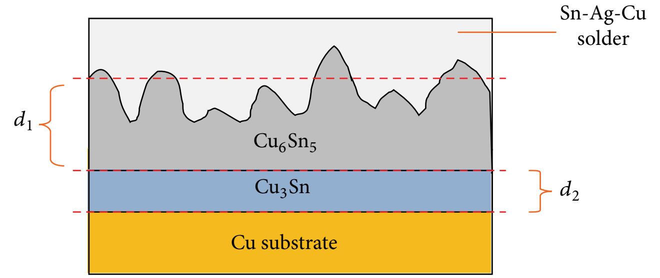

Figure 9: Schematic diagram of IMCs thickness measurements, with d_1 as the thickness of Cu_6Sn_5 and d_2 as the thickness of Cu_3Sn.

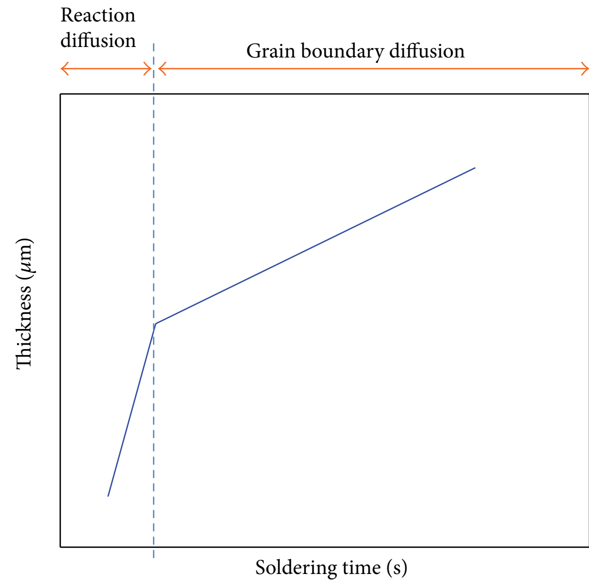

Figure 10: Growth mechanisms of IMC layer during soldering process.

Cu_6Sn_5 in the liquid solder. Both the Ag_3Sn phase and Cu_6Sn_5 compounds were detected in the solder matrix of Sn-Ag-Cu/Cu after soldering for 30 s. The Cu_6Sn_5 became coarser with increasing Cu content.

After prolonged soldering for 180 s, a thin Cu_3Sn layer was formed between the Cu_6Sn_5 layer and Cu. Moreover, the IMC layers became thicker, and the number of the IMC grains decreased when the samples underwent soldering for 600 s, which resulted in a scallop-like morphology.

Figure 11 demonstrates the growth of Cu-Sn IMCs at varying reflow times. Figure 11(a) shows the formation of a scallop-type structure at the interfacial layer of SAC305/Cu when the reflow time was 30 s. Ag_3Sn are present in the solder matrix. Furthermore, spalling of Cu_6Sn_5 spheroids was observed because the Sn concentration in SAC305 was high. The formation of the spheroids was assisted by the ripening reaction among the compound grains. When soldered for 180 s, a thin band of Cu_3Sn were observed at the Cu_6Sn_5/Cu interface (Figure 11(b)). When soldered for 600 s, the IMC layers became thicker, and the number of scallop

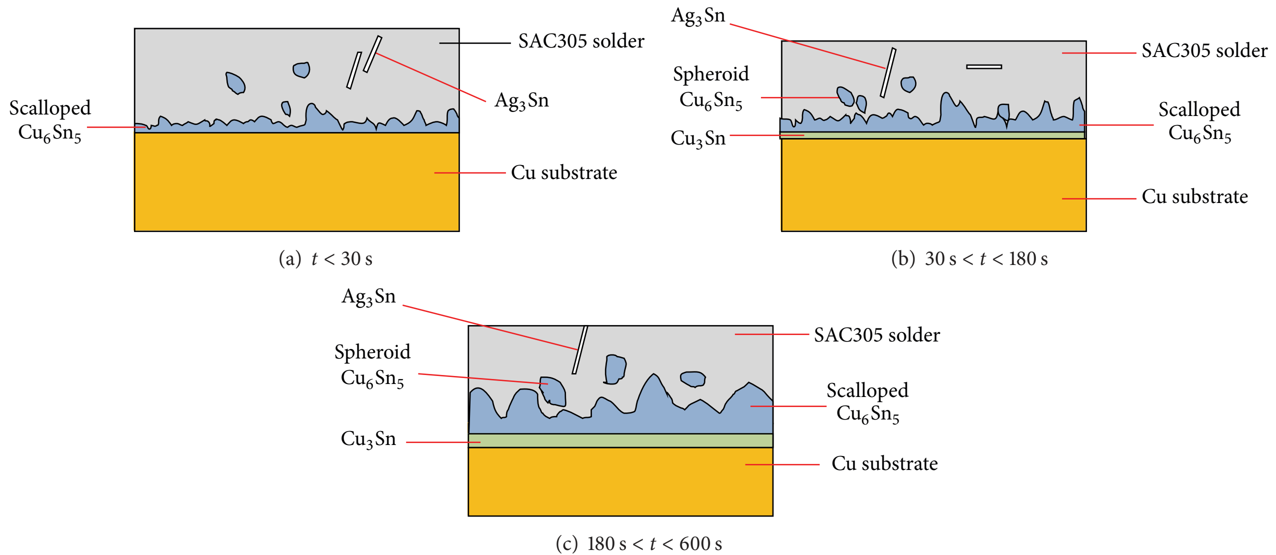

FIGURE 11: Growth mechanism of Cu-Sn IMCs at various reflow times: (a) formation of scallop Cu_6Sn_5 at the SAC305/Cu interfacial region, (b) appearance of Cu_3Sn between the Cu_6Sn_5/Cu interface, and (c) increase in both Cu-Sn IMCs thicknesses with increasing reflow times.

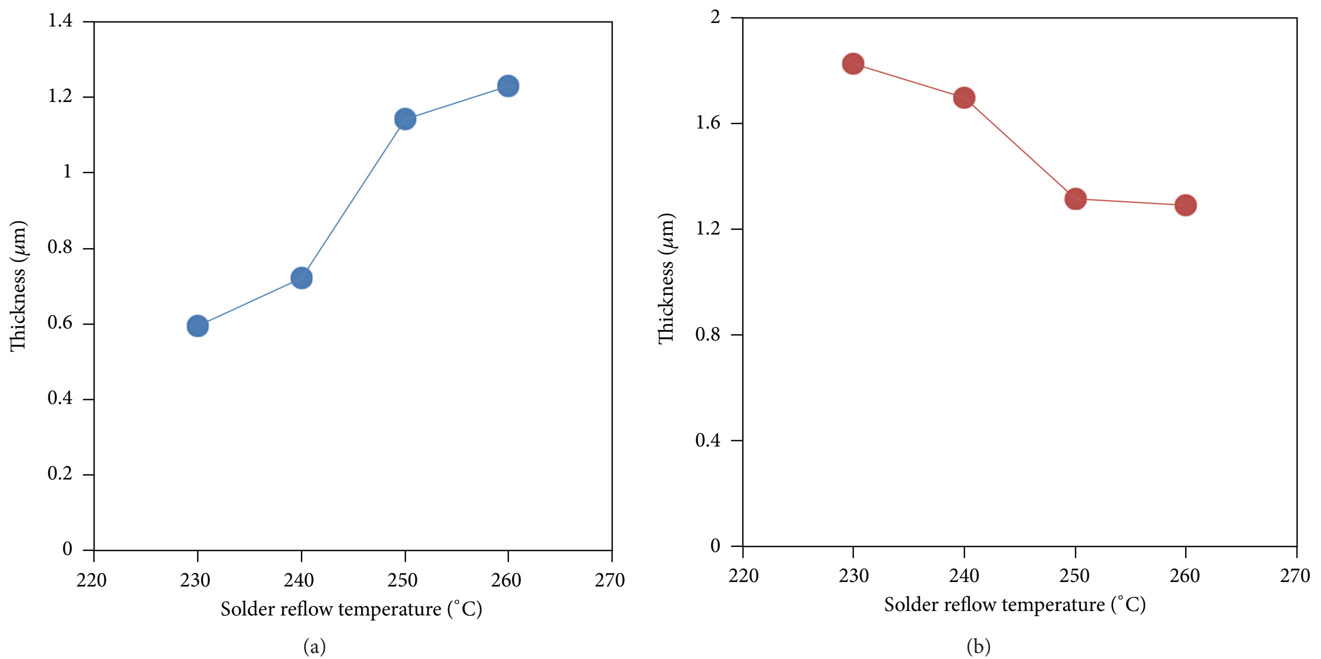

FIGURE 12: (a) Cu_3Sn and (b) Cu_6Sn_5 IMCs thickness as a function of reflow temperature at a reflow time of 30 s.

Cu_6Sn_5 decreased. Cu_3Sn maintained its continuous layer-like morphology with increasing thickness and reflow time (Figure 11(c)).

Li and Chen [63] also conducted an experiment on commercial lead-free solders, namely, Sn-3.5Ag and Sn-3.5Ag-0.7Cu, by using a standard infrared reflow oven at 250°C for 2, 6, 15, 30, 60, 120, 240, and 360 s. Both Cu_6Sn_5 and Ag_3Sn were detected in the solder joint. The Ag_3Sn phase was detected because it was formed on top of the layer during the reflow process. However, a scallop-like layer of Cu_6Sn_5 IMC was located at the solder-Cu substrate interface. The authors added that Cu_3Sn phase was not observed in the as-solidified solder joint, although it may exist between Cu and the Cu_6Sn_5 phase.

Figure 12 compares the thicknesses of the IMC layers formed at the interfacial region as a function of reflow temperatures. The Cu_3Sn intermetallic layer consistently increased with increasing temperature (Figure 12(a)), whereas Cu_6Sn_5 gradually decreased with increasing reflow temperature (Figure 12(b)). Figure 13 shows the relationship between the IMC layer thickness and the reflow time. Likewise, at a specific soldering temperature, the thickness

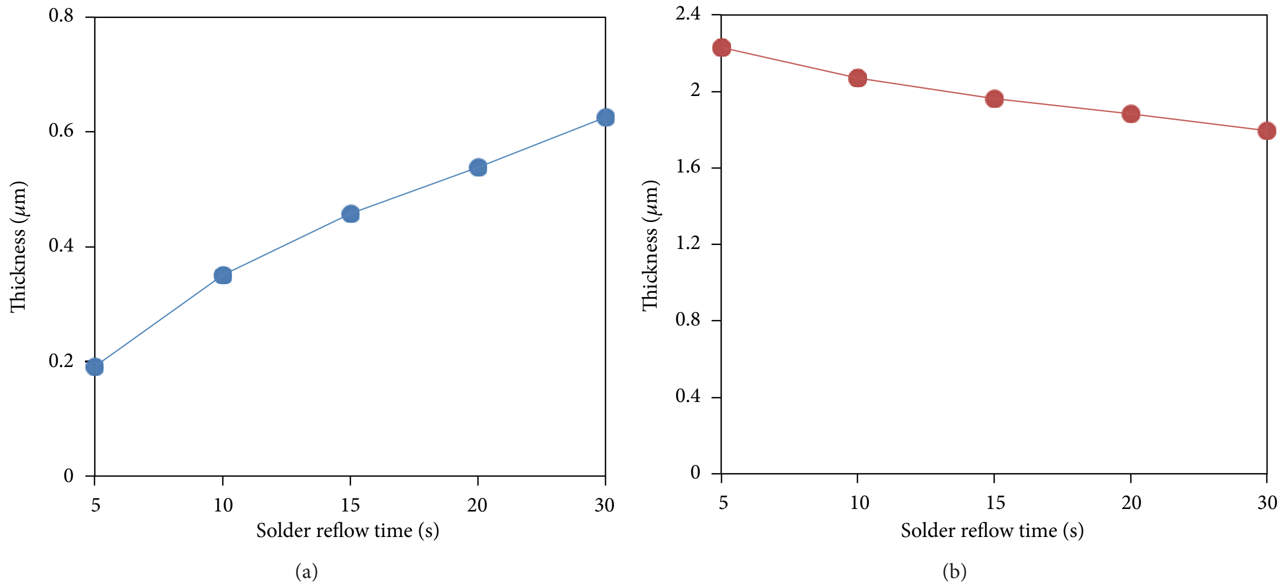

FIGURE 13: (a) Cu_3Sn and (b) Cu_6Sn_5 IMC layer thickness versus reflow time at 230°C.

of the IMC layers at the interfacial zone increased with increasing soldering time. Based on the study done by Yu and Wang [3], the increase in soldering time enables the IMC layer to grow quickly because of the precipitation effect of Cu_6Sn_5. Cu_6Sn_5 could be recalled to develop into Cu_3Sn when the Sn supply is limited. Hence, the Cu_3Sn thickness increases with decreasing Cu_6Sn_5 thickness despite the fact that Cu_6Sn_5 generally grows with increasing solder time. These results provide evidence that the interfacial Cu_3Sn layer grows at the expense of Cu_6Sn_5 according to the reaction $Cu_6Sn_5 + 9Cu \rightarrow 5Cu_3Sn$ [29]. Moreover, the Cu_3Sn thickness growth follows a linear equation. According to material kinetics, a linear growth indicates that the formation of the interfacial Cu-Sn IMC layer is an interfacial reaction-controlled process [64].

The increase in the Cu_3Sn IMC layer results from the diffusion and reaction type growth during the soldering process [17]. The growth of Cu_3Sn consists of several steps: the dissolution of Cu from the Cu pad, the diffusion of Cu and Sn through the existing Cu_3Sn layer, and the conversion of Cu_6Sn_5 into Cu_3Sn at the Cu_6Sn_5/Cu_3Sn interface and the reaction of Sn with Cu at the Cu/Cu_3Sn interface [65]. Conversely, Cu_6Sn_5 is formed by the dissolution of Cu, followed by a chemical reaction [17], and its growth is restricted by the Cu_3Sn layer because the amount of free Cu atoms that can diffuse to the Cu_6Sn_5 is very small. Therefore, Cu_3Sn grows rapidly with temperature, consuming Cu_6Sn_5 at the interface of Cu_3Sn/Cu_6Sn_5.

8. Conclusions

Sn-Ag-Cu is the leading candidate for the fabrication of ecofriendly products. Two intermetallic layers are commonly found at the interfacial zone of Sn-Ag-Cu and the Cu substrate, that is, Cu_6Sn_5 and Cu_3Sn. Cu_6Sn_5 forms first and possesses a scallop-like structure, whereas Cu_3Sn emerges at the Cu_6Sn_5/Cu interface and has a layered structure. However, the thickness of Cu_3Sn is much smaller than that of Cu_6Sn_5, and its formation requires longer contact times. Morphological transformations could occur depending on the phase stability. Both Cu-Sn IMCs grow with increasing reflow temperature and time.

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