INTERFACIAL REACTION OF SN-BASED SOLDER JOINT IN THE PACKAGE SYSTEM

by

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Abstract

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Now a day in electronic industry, as the trend of requiring smaller package size with better electronic performance, lead-free solder joints are always required to decrease their sizes. As a result, the reliability of smaller size solder joints has became a critical issue. The primary factor causing the reliability issue of lead-free solder joints is intermetallic compound (IMCs) formation which forming during soldering process and thermal aging process and can significantly affect the mechanical properties of solder joint. In this study, two different size solder joints with same composition (SAC305 with 96.5%Sn, 3.0Ag, 0.5%Cu) are subjected to isothermal aging treatment in 150℃ for 0-500 h to evaluate the effect of the solder size on IMC formation. Interfacial reaction in the Cu/Sn and Cu/Ni/Sn interface are observed. Two different phases of IMCs including Cu_6Sn_5 (η phase) and Cu_3Sn (ε phase) were founded in the Cu/solder interface. The morphology of the IMC layer was analyzed by scanning electron microscopy (SEM). Growth thickness and growth kinetics of the intermetallic compound were studied. The result showed that during solid state aging treatment, the IMCs forming in both small and large solder joints are diffusion-controlled. The growth rate of IMCs in small solder joint is faster at early aging period, and then its growth rate decreases and becomes slower than large size solder joint. The different of the IMCs growth rate can be explained by the Cu-Saturation in the solder reflowing process. Furthermore, Ni layer acts as a very effective diffusion barrier which decreases the growth rate of Cu/Solder IMCs.

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Chapter 1

Introduction

Solder joint plays an important role in electronic packages of electronic customer products, acting both as electrical interconnections between chip and components, and also as mechanical support for components. In nowadays, as the industry want to provide smaller products with higher electrical performance, which means higher I/0-density and smaller solder size, fine pitch solder joints are required, and therefore, the reliability of smaller solder joint becomes an serious issue. A very important factor that can influence the reliability of solder joint is the intermetallic compound (IMCs) forms at the interface of solder and its substrate. Usually, intermetallic compound begin to form at the reflowing process when the solder is forming. It continues to growth to thicker during room temperature storage and more rapidly in the thermal annealing. The growth of IMC can have a significant impact on the properties of solder joint, influence the strength and result in mechanical failure of the joint [1-5] For example, P. L. Tu and Y. C. Chan reported that fatigue lifetime of solder joint decrease linearly ith the increasing square root of IMCs layer thickness [6].

With the reduction of solder volume and solder height, microstructure changes in the solder joint and the growth mechanism of intermetallic compound become highlighted. Many related questions need to be answer, such as are different size solder grow in different rate? Do IMCs in solder joint of different size grow in the same kinetics? In previous research, IMC growth rate and its impact have been deeply invest in “as-reflowed ” solder joint. Bo Wang and Fengshun Wu have reported that the solder joints with lower solder height have a faster IMC growth rate [7]. While B. Salam and N. Ekere reported that the increasing solder size does not significantly affect the growth of the intermetallic layer thickness [8].

In this thesis, I report a study on the effect of the solder size on intermetallic layer formation by comparing the morphology change and growth rate of two different size solder joint aged at a same temperature for different aging time. The layer thickness and microstructure were analyzed using scanning electron microscopy (SEM). Photoshop was used to measure the thickness of intermetallic compound. Two different size of solder joints with composition of Sn-Ag-Cu (305) were used.

Chapter 2

Background

In this chapter, fundamental knowledge of solder joint technology, including lead-free solder joint, surface mounted technology, pin-through-hole technology, flip chip technology and their application are first included.

Then, reactions of intermetallic compound formation happened in lead-free solder joint during both wetting reaction and solid state reaction are introduced.

2.1 Solder Joint Technology

2.1.1 Lead-free Solder Joint

Solder joint technology has been used in electronic packaging industry for making the interconnection between electronic components for long time. The process that solder joint accomplish is to joining the solder with copper parts by forming intermetallic compounds in a chemical reaction.

Tin/lead alloy used to be the primary materials of solder joint. Tin-lead (SnPb) solder is a eutectic alloy, which has melting temperature of 183℃.It can form a metallic bond with Cu at such a low temperature, which make SnPb to be a ideal solder material used widely. However, the toxicity of Pb which make the use and disposal of Pb containing electronic product become a serious environmental issue [9]. In United State, for anti-Pb bills are pending in the congress, including one from the Environmental

Protection Agency. In European, the agency of Waste from electrical and Electronic Equipment (WEEE) issued a directive calls for a ban of Pb-containing solder in all electronic consumer products from July, 2006 [10]. China, Korea and Japan has also proof related rules of elimination Pb from electronic industry. Environmental concerns of the use of Pb-Sn solders provide a strong driving force of study of the environmental friendly materials, Pb-free solder joint [11,12].

Most of the eutectic Pb-free solders are Sn-based. There have been some candidate include alloys consisting of Sn and noble metals such as Au, Ag, Cu and Bi, Cd, In, Sb or Zn [13,14]. Several studies has been reported, but there are still no ideal replacement materials with respect to reflow temperature, reliability of solder joint, and assembly cost [15]. Eutectic Sn-noble metal alloys always have a high melting point which leads to high reflowing temperature, as shown in Table-2.1, causing thicker IMC formation and larger strain at the joint during assembling process. These can cause very serious reliability issue such as delamination and fatigue the solder joint.

Zinc (Zn) is cheap and easy to find. Eutectic Sn-Zn has a relatively low melting point compare with other Pb-free solder alloy, which is closest to eutectic Sn-Pb. But Sn-Zn alloy cause too many difficulties in soldering process because it can forms a very stable oxide rapidly. Bismuth (Bi) has very good wetting properties while it is hard to get because the main source of Bi is a by-product in Pb refining. Indium (In) is too expensive. Antimony (Sb) has been recognized as a toxic metal by the United Nations Environment Program. Sn-Ag has too large two phase regions. Sn-0.9Cu, Sn-3.5Ag, and Sn-Ag-Cu. has been looking as promising solder alloys based on the selection criteria. The most promising one is the ternary Sn-Ag-Cu eutectic (217℃) as its relatively low melting temperature, good quality solder joint forming with Cu substrate, superior mechanical properties and good compatibility with other components [16]. The international Printed Circuit Association has suggest that 96.5Sn-3.0Ag-0.5Cu (SAC305) will be the most widely used alloys in the future [17].

Table 2-1 Binary Pb-free Eutectic Solders

Systems	Eutectic temp. (°C)	Eutectic composition (wt%)
Sn-Cu	227	0.7
Sn-Ag	221	3.5
Sn-Au	217	10
Sn-Zn	198.5	9
Sn-Pb	183	38.1
Sn-Bi	139	57
Sn-In	120	51

2.1.2 Surface Mount Technology

Wire bonding technology has been widely used to connect Si chip to leadframe substrate in most of the portable electronic consumer product such as mobile phone and computers. In wire bonding technology, solder joints are used to join the bond pads on a packaging circuit board to the legs of the leadframe. Figure 2.1 shows the wire bonding between a Si chip and a Cu leadframe substrate.

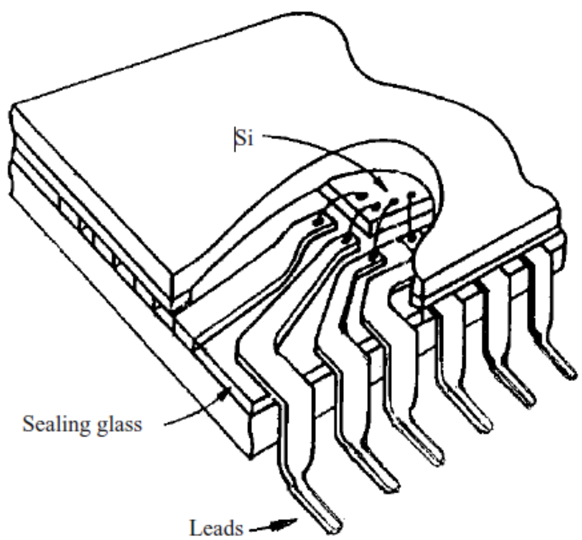


Figure 2- 1 Schematic Diagram of Wire Bonding Between A Si Chip and A Leadframe [10].

Solder joint in surface mount technology is fabricated by printing a pattern of a lots of solder paste on a bond pads, the legs of leadframe are placed on a printed paste mount. Then the assembly will be putted on a belt which can move in a tube furnace. The joint will be formed in melting temperature and a forming gas ambient.

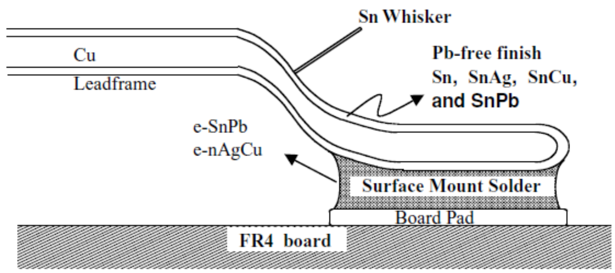


Figure 2- 2 Schematic Diagram of a Surface Mount Solder Joint Connecting a Leg and a Substrate [10].

Solder joint in surface mount technology between a leg and a substrate board can be showed by Figure 2-2.The “reflow” in solder forming means the heating process, the temperature is above the melting point of the solder alloy by 30 to 40 ℃ for about half minutes. In this period, the solder joint get melted and react with the substrate and the bond pad to form a metallic joint. The leadframe will be coated with a thin layer of eutectic SnPb for easier achieving the joining of all the legs in the half minute reflowing time. While due to the environment problem causing by Pb, the coating has been alternate by Pb-Free material as pure Sn or Sn-Cu eutectic alloy. However, Sn whiskers which can cause electrical shorts between legs have been found on these coating. Other reliability issues such as cracks happen on the solder and leg interface have also been found.

2.1.3 Pin-Through Technology

Pin- through-Hole technology can provide better mechanical reliability by using straight legs so that the legs can act like pins that can be inserted into holes drilled in the board. The holes on the board is plated with immersion Sn and Cu, so that in reflowing process, the molten solder can wet the immersion Sn and rise along the holes by capillary force. Then the pins can be soldered on the board through the holes. Although Pin-through-Hole technology can provide better mechanical reliability, its application is limited for the high cost. Figure 0-3 shows the cross-section area of through holes plated with Cu and immersion Sn.

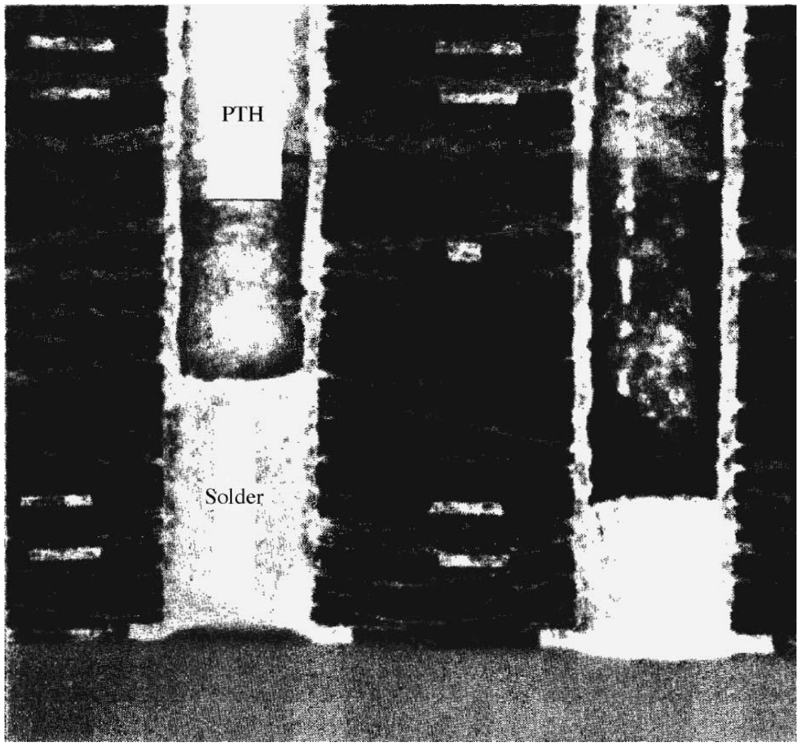


Figure 2- 3 Cross-Sectional Image of Through Holes Plated with Cu And Immersion Sn.

2.1.4 Flip Chip Technology

Flip chip technology is a method of forming electronic connections between Si chip and printed circuit board or ceramic module. The electronic connections can be achieved through an area array of solder joints between the Si chip and the substrate by flip the Si chip and make the circuit faces the substrate. The solder joint in flip chip technology can cover all or at least a large area of the surface of the chip, while in surface mount technology, connections can only formed on the periphery of the chip. Figure 0-4 shows an area array of solder balls on the Si chip.

There are mainly three steps in flip chip joints formation process. Firstly, solder is bumping on a Si chip by electroplating or stencil printing, then reflow the solder to make the bumps into balls. Secondly, flip the chip and make the circuit faces the substrate to bond the chip to its substrate. Finally, use the epoxy to fill the gap between Si chip and the substrate.

Comparing to other solder joint technology, flip chip technology can provide smaller packaging size, higher input / output (I/O), better performance of the device. Thus, it has been widely used in mainframe computers such as a server and handhold devices such as telephone.

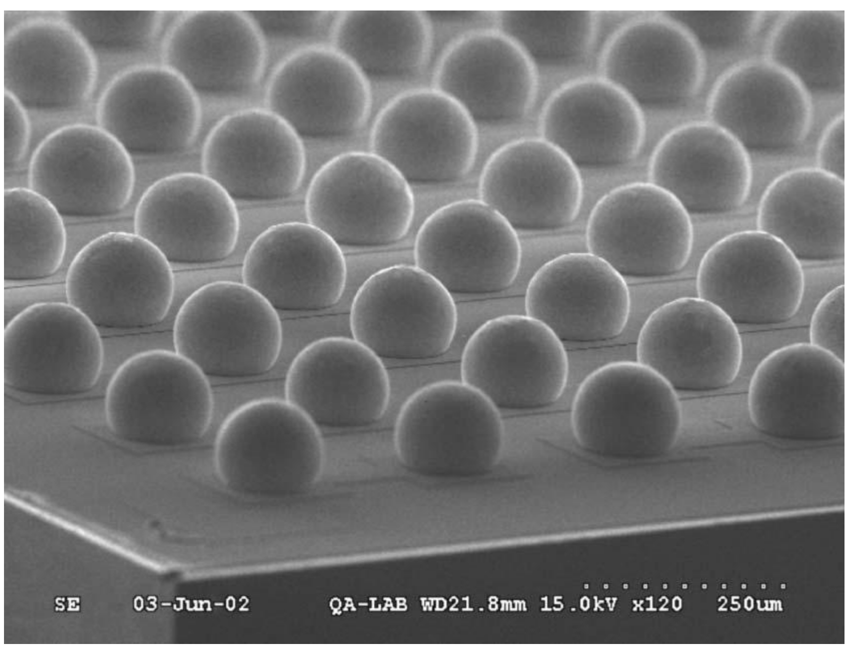


Figure 2- 4 An Area Array of Solder Balls on The Si Chip

2.2 IMC Formation in Pb-Free Solder Joint (or Copper-Tin Reactions)

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). 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.

Usually, the sample has been reflowed for several times before solid-state aging test. So there must be certain scallops-type Cu_6Sn_5 formed before aging. In solid state aging process, the morphology of Cu_6Sn_5 changes from scallop-type to layer-type. The IMC formed in solidsate aging need to be determined by subtracting the amount of IMC formed during reflow process. The average thickness of IMC layer can be obtained by dividing the total cross-sectional area of the IMC by the total length.

In solid-state reactions, the IMC has layer-type morphology. The kinetics of the IMC growth can be diffusion-controlled or interfacial-reaction controlled. In high enough temperature, all the IMCs obey a diffusion-controlled growth, so the ratio of thickness among the layers is proportional to the ratio of the square root of the interdiffusion coefficient in each layer.

While in wetting reaction, the Cu_6Sn_5 has scallop-type morphology, and the growth thickness is found to be $t^{1/3}$ dependent on time. Which means the kinetics of the scallop-type Cu_6Sn_5 is not diffusion-controlled or interfacial-reaction-controlled. It is indicated to be a ripening reaction and obey the kinetics named as supply-controlled growth kinetics.

2.2.1 Wetting Reaction

Soldering is a metallurgical joining process that bonding solder to a metal substrate in a certain temperature. For lead-free solder joints, which usually have high concentration of Sn, the soldering reaction is basically between Sn and the Cu substrate. For SAC305 solder alloy, during soldering process, SAC305 melts and meet Cu substrate, Sn from the melting solder get react with Cu and forming intermetallic compound (IMC) at the interface of Cu and Sn. Thus, the IMC layer bond Cu and Sn together [18-23].

Generally, the wetting process can be divided into three stages (see Figure 2-5.).

Spreading;

When heated, solder melted and spread out on Cu substrate to form a cap on it.

Base metal dissolution;

In this process, Cu atoms from the substrate dissolve into molten solder, substrate remain to be solid and does not change its microstructure.

Formation of an IMC layer.

The dissolved Cu atoms and liquid solder react and form an intermetallic layer. The liquid solder phase transformed to some solid phases when the joints get cooled. The kinds of solid phases forming in this process are related to the properties of achieved solder joint.

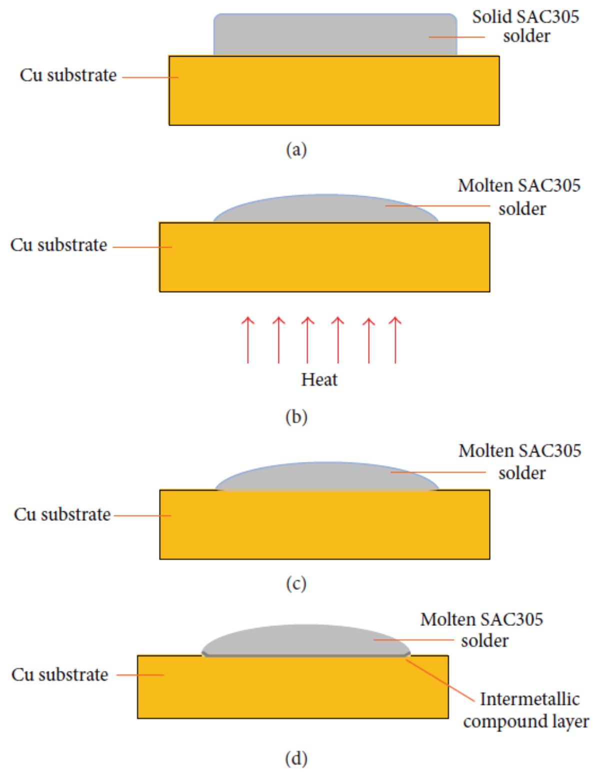


Figure 2- 5 Solder Wetting Process: (A) SAC305 Solder on The Cu Substrate, (B) Liquid Solder Spreading Over the Cu Substrate During Soldering, (C) Cu Diffuse in the Liquid Solder, and (D) Cu Reacting with the Liquid Solder to form an Intermetallic Compound Layer [24].

In the reflow process, solder joint on the chips must join the UBM successfully, or spalling of the intermetallic compound will occurs which could cause reliability issue.

2.2.2 IMC Formation in Wetting Reactions

During wetting process, solder is heated to melting temperature, Cu from the substrate dissolves into molten solder very fast. The Cu dissolve in a non-equilibrium process, Cu with a very high concentration quickly localize in the interface of Cu substrate and molten solder until the solder getting supersaturated with Cu. After Cu saturated in the interface of Cu/molten solder, a large driving force for the chemical reaction between Cu and Sn exist in the interface, a thin layer of Cu_6Sn_5 IMC start to form. The Cu_6Sn_5 formed in wetting process has scallop-type morphology and the rate of formation is very fast comparing with the Cu_6Sn_5 forming in solid state aging process [25]. The growth kinetics of Cu_6Sn_5 in this process is a unique one, we will discuss it later. If the reflow time is long enough, layer-like IMC Cu_3Sn can be found between Cu_6Sn_5 and Cu substrate by diffusion and reaction type growth [26]. The IMC growth mechanism can be schematically illustrates by Fig 2-7.

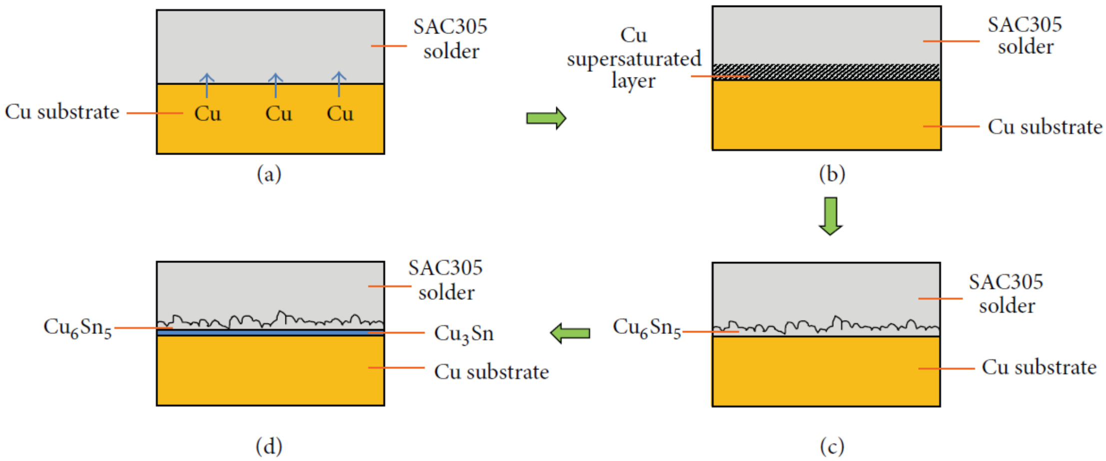


Figure 2- 6 Scheme of the Interfacial Reaction of SAC305/Cu During Solder Reflow: (A) Dissolution of the Cu Substrate, (B) Supersaturating of the Molten Solder Layer with Cu, (C) Formation of the Scallop-Type Cu_6Sn_5 at the Interface, and (D) Cu_3Sn Emerges Between Cu_6Sn_5/Cu with Prolonged Soldering.

Now let's briefly talk about the growth kinetics of IMC growth in wetting reaction. There are several different opinions about the dominant growth kinetics of Cu_6Sn_5 during the time of reflow.

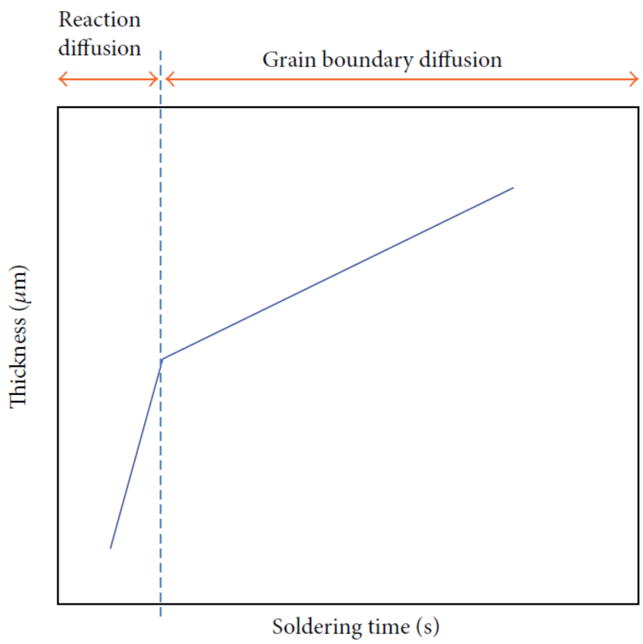


Figure 2- 7 Growth Mechanisms of IMC Layer during Soldering Process

Additionally, King-Ning Tu concluded that the growth of Cu_6Sn_5 is dominant by neither diffusion-controlled nor interfacial reaction controlled kinetics. It obeys a kinetics which is named supply-controlled growth kinetics. It was indicate that the thickness of the scallops has a $t^{1/3}$ dependence on time, with the time increasing, the scallop IMC growth bigger but fewer. So it does not obey the diffusion-controlled or interfacial-controlled kinetics. A non-conservative ripening reaction is happened among the scallop-type Cu_6Sn_5 grains.

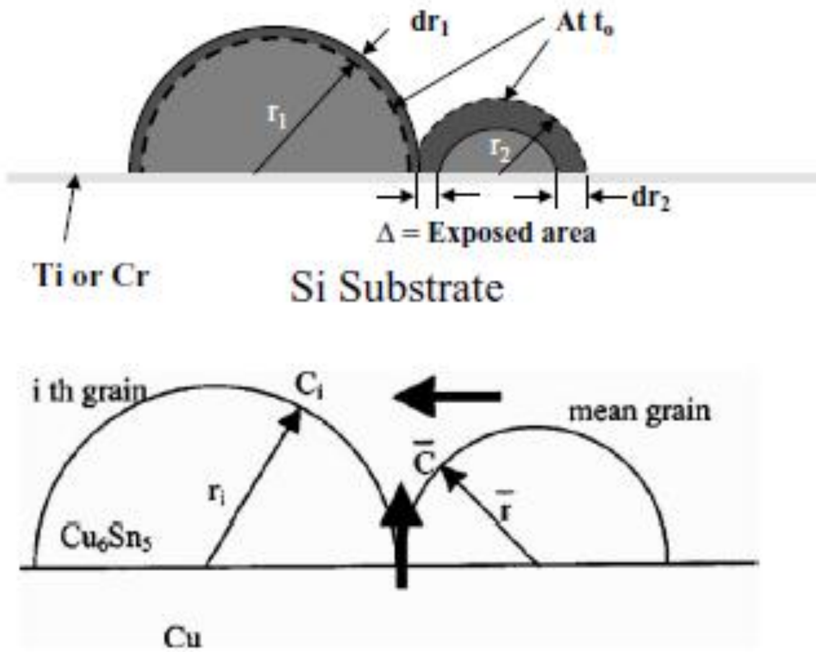


Figure 2- 8 Schematic Diagram of Cross Section of Two Neighboring Scallops.

Figure 2-8 shows a schematic diagram of the cross section of two scallop Cu6Sn5 forming in wetting reaction. For simplified the discussion, we assume there is no Cu3Sn forming in between Cu6Sn5 and Cu substrate. In wetting process, when solder is heated to over 200℃, molten solder turns to liquid phase. The diffusivity of Cu in liquid solder is about 10-5 cm2/sec. The Cu flux (showed by the vertical arrow) diffuses through the valley between the two Cu6Sn5 scallops rapidly and then reacts with Sn in front of the scallops (showed by the horizontal arrow.). The diffusion of Cu through the valley of scallops is very fast, on the order of 10-5 cm2/sec, and the diffusion distance is very small, Cu diffusion is not a rate-limiting step. However, the Cu atoms under the valley can be consumed very soon, then a lateral diffusion from the Cu nearby will happen. The diffusion rate is very fast too, and it is not a rate-limiting diffusion too. The activation energy was found to be 0.2 to 0.3 eV/atom, which is very low compare to the activation energy of the growth of Cu6Sn5 in solid state reaction. Due to the experiment reported by King-Ning Tu, to achieve same thickness (a few centimeters) of Cu6Sn5, in the wetting reaction in 200℃, it only takes a few minutes, but in solid-state aging process in 170℃, it took 1000hr. Showing that wetting reaction is four orders of magnitude faster than the solid state aging although there is a temperature difference of 30℃ which is not very big. Thus, the wetting reaction is a much faster kinetics process, which has been defined to be supply-controlled growth kinetics

2.2.3. IMC formation in Solid-State Reactions

Although we want the growth of the intermetallic compounds to stop right after the wetting reaction, because the thick IMC layer can have a negative impact to the reliability of the Pb-free solder. But the device is always working in a high operation temperature, that solid-state reaction will happen and influence the thickness and morphology of the IMC layer.

So it is very necessary to study the mechanism and kinetics of IMC layer growth in the solid-state aging reaction.

In solid-state aging reaction, two layer of intermetallic compound could be formed, Cu_6Sn_5 near solder and Cu_3Sn near Cu substrate. The kinetics of IMC layer growth can be diffusion controlled or interfacial reaction controlled. Generally, the growth kinetics of IMC layer can be determined by plotting the measured IMC layer thickness against the exposure time at a certain annealing temperature. The thickness can be expressed as a function of aging time using the time power law equation as [27]:

$$x = x_0 + A \cdot t^n \qquad (1)$$

Where x is the IMC layer thickness at time t, x_0 is the layer thickness after reflow process, n is a constant or called time exponent that indicate intermetallic compound growth mechanism, A is the temperature dependent growth constant, which can be describe by Arrhenius type equation as shown below:

$$A = A_0 \cdot \exp\left(-\frac{Q}{RT}\right) \qquad (2)$$

Where A_0 is a pre-exponential factor, Q is the activation energy of the growth, T is the absolute temperature and R is the universal gas constant (8.314 J/K·mol)

Combining (1) and (2) together, IMC thickness becomes:

$x = x0 + A0 \cdot tn \cdot \exp(-\frac{Q}{RT})$ (3)

If the growth of IMC layer is a diffusion controlled process, n is on the order of 0.5 [28], the IMC layer kinetics can be described by the square root time law. The thickness of IMC layer can be measured a d plotted against the exposure time, at any given temperature. Vianco et al [29] has found that for the total intermetallic layer pure Sn, Pb-Sn, and two kinds of Sn-riches solders (96.5Sn-3.5Ag and 95Sn-5Sb), the time exponent is about 0.5 in lower annealing temperatures (below 135℃) and close to 0.4 at higher (more than 170℃) annealing temperatures.

In the solid-state aging process of Sn-based Pb-free solder alloy, there can be two main species of IMC layer formed, Cu6Sn5 (η phase) and Cu3Sn (ε phase). The mechanisms of IMC formation are influenced by the interdiffusion characteristics of Cu and Sn. Some experiment on Cu-Sn system has showed that interstitial of Cu is dominant in lower temperature (below 170℃) and vacancy diffusion of Sn is dominant in higher temperature (over 170℃)[30,31]. Which means Cu diffuse faster than Sn when the annealing temperature is below 170℃. In that condition, in the Sn-Cu interface, Cu can react with diffusion Sn to form Cu6Sn5and Cu3Sn. Cu can also react with Cu6Sn5to form Cu3Sn. Which means the growth of the two IMC layer is influenced by the synergy function which means Cu_3Sn forms at an expense of Cu_6Sn_5.

The solid state interfacial reactions occurring in Sn-Cu interface can be describe as:

$$6Cu + 5Sn \rightarrow Cu_6Sn_5 \qquad (1)$$

$$3Cu + Sn \rightarrow Cu_3Sn \qquad (2)$$

$$9Cu + Cu_6Sn_5 \rightarrow Cu_3Sn \qquad (3)$$

As we can see in Figure.2-9, Cu_6Sn_5 (η phase) has a lower Gibbs free energy than Cu_3Sn, showing that Cu_3Sn has a higher activation energy and less driving force than Cu_6Sn_5, so Cu_6Sn_5 can forms earlier Cu_6Sn_5r than Cu_3Sn in lower solid state aging temperature (below 170 ℃). .

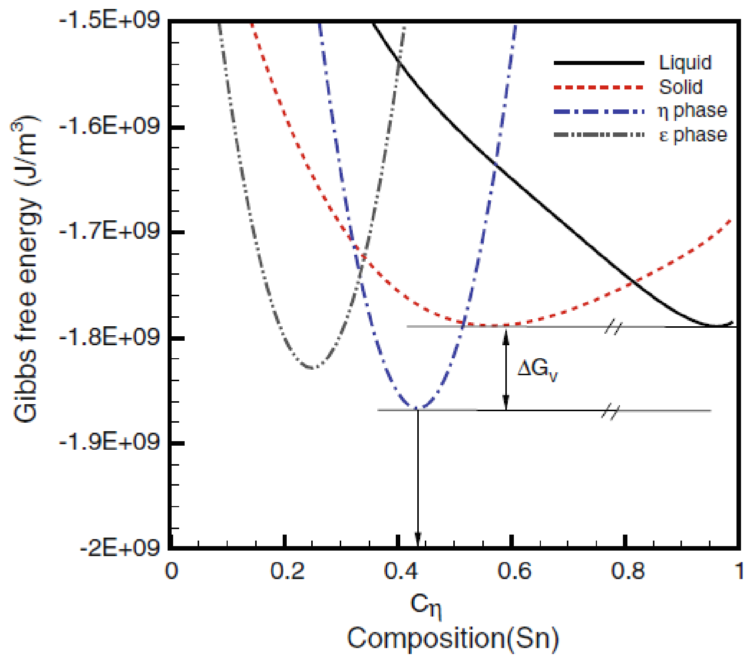
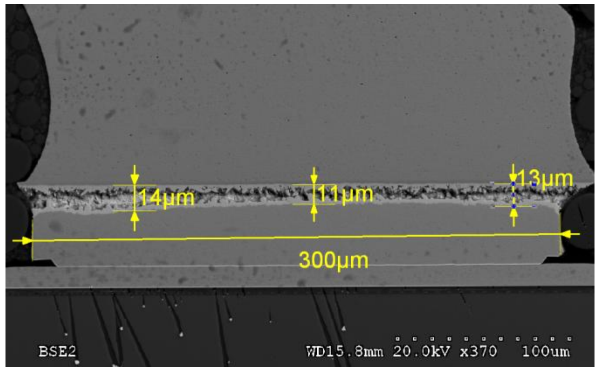


Figure 2- 9 Comparison of Gibbs Free Energy of Cu_6Sn_5 and Cu_3Sn.

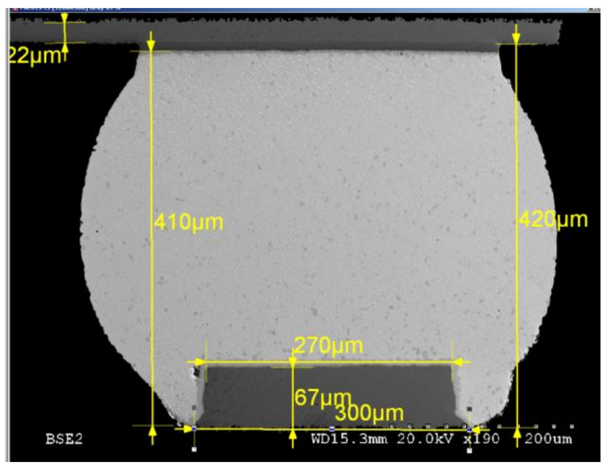
Chapter 3

Experimental Procedure

In this study, two different size solder joints with the same composition (SAC305 with 96.5%Sn, 3.0% Ag, 0.5%Cu) were used. The large solder joint has a ball shape with Cu/Ni/Sn/Cu structure. The small solder joint has a pillar shape with Cu/Ni/Sn/Cu structure. The stand-off height of large solder bump is around 343μm and small bump around 12.5μm. The ratio of height to length of the solder joint is 1.27 in large, while 0.04 in small. The size difference between small and large specimens is very significant.



(a)



(b)

Figure 3- 1 Microstructure of Small (A) and Large (B) Solder Bump.

The two pictures in figure 3-1 show the microstructure of small solder joint and large solder joint. Samples were subjected to isothermal aging treatment in 150℃ for 500h. After the aging treatment, samples were mounted by epoxy and very fine polished to detect the cross section area. To better identify the IMC layer, sample were etched by 97per cent methanol and 3 per cent HCl (vol.%) solution for about 5 s to selectively remove the Sn solder alloy.

Scanning electron microscopy (SEM) in the back scattered electron (BSE) mode was used to observe the microstructure of the samples. Energy dispersive X-ray spectroscopy was used to analyze the composition of the IMC and solder joint. Software “PHOTOSHOP7” was used to measure the average thickness of IMC, based on the BSE images.

Chapter 4

Morphology Change of Solder Joint during Thermal Aging

4.1 Morphology Change in Small Solder Joint in Thermal Aging

Figure 4-1 shows the BSE pictures taken for small solder joints during different aging times. As we can see from the pictures, the IMC layers at both top and bottom side grow thicker as aging time increasing. The shape of the IMC goes from scallop-type to planer-type.

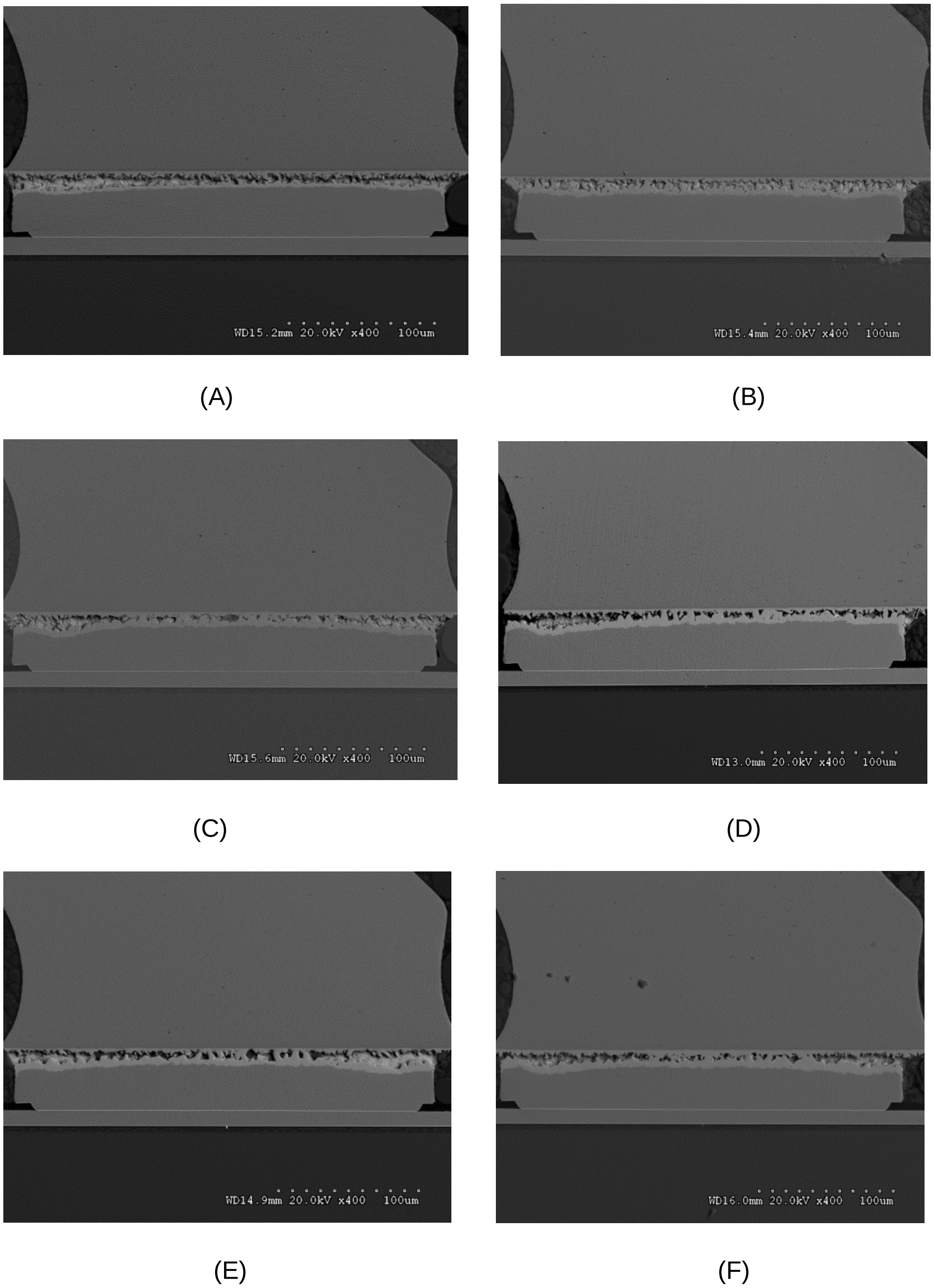


Figure 4- 1 Microstructure Change of the Small Bump by Aging (A) 0hr (B) 48h (C) 72h (D) 150h (E) 250h (F) 500h

The BSE pictures in Figure 4-2 are taken in larger magnification which show more detail of the surface morphology. As we can see in the pictures, two different IMC have formed during aging period. Cu_6Sn_5 forms at the early aging period, which continues growing thicker as the aging time increasing. When the aging time get longer, Cu_3Sn forms in the interface of Cu_6Sn_5 and Cu substrate at the bottom IMC layer.

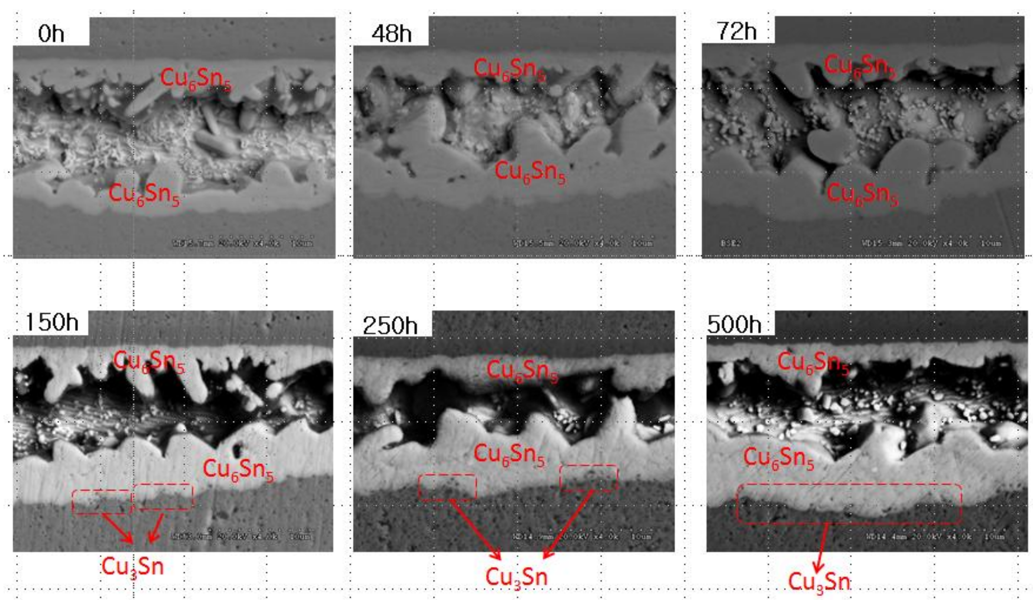
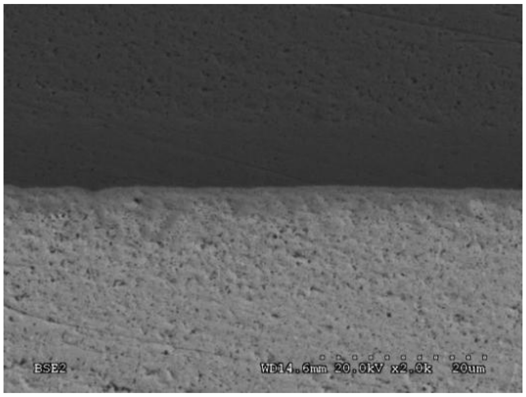


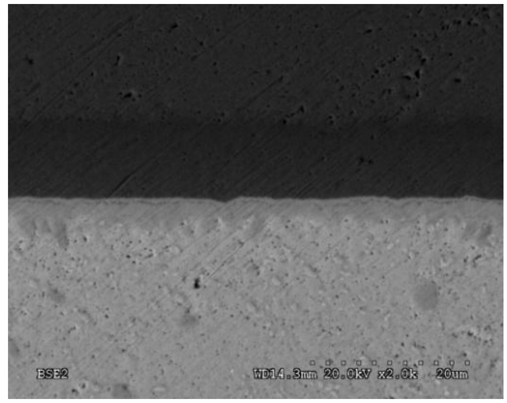
Figure 4- 2 The Growth Behavior of Cu_6Sn_5 and Cu_3Sn during Aging Time

4.2 Morphology Change in Large Solder Joint in Thermal Aging

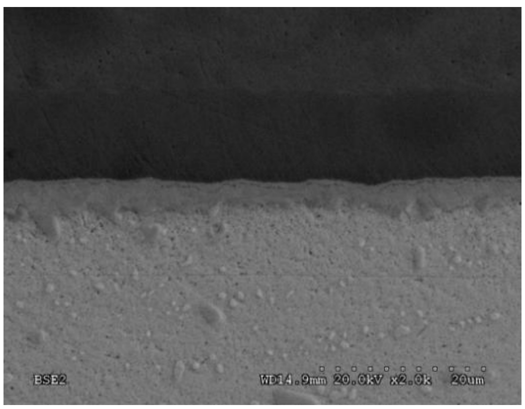
Figure 4-3 shows the BSE pictures taken for the top layer of large solder joints during different aging times. As we can see from the pictures, the IMC layers at top side get thicker during increasing aging time. The shape of the IMC goes from scallop-type to planer-type.



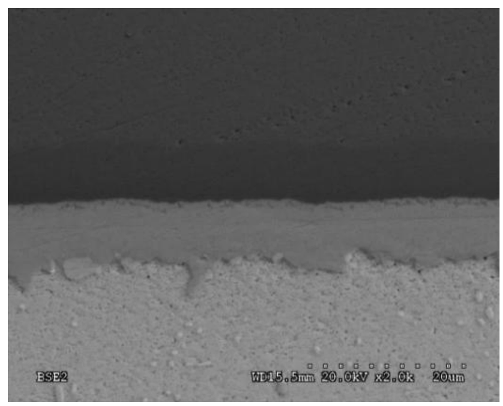
(A)



(B)

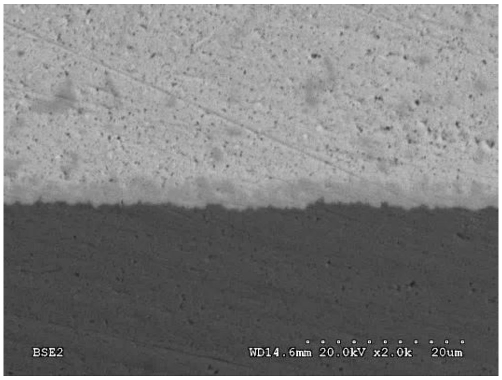


(C)

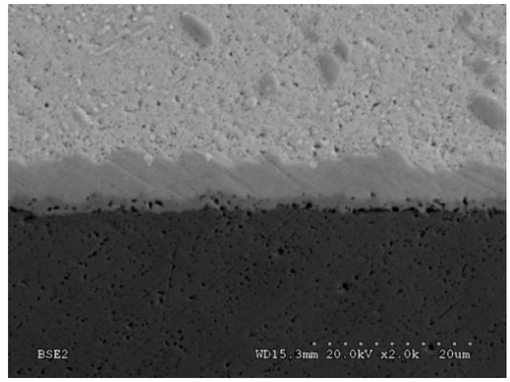


(D)

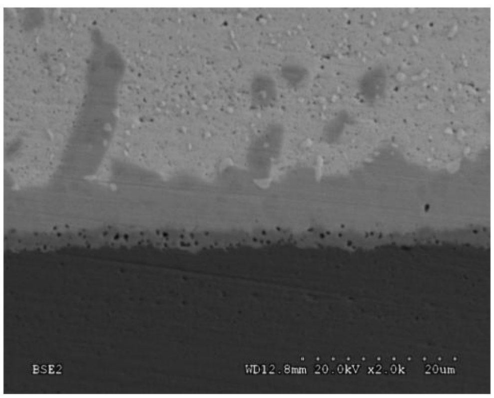
Figure 4- 3 Top Layer IMC Forming in (A) 0h (B) 150h (C) 500h (D) 2000h Aging Time



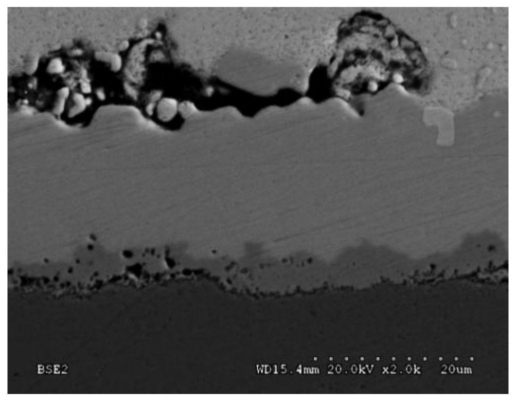
(A)



(B)



(C)



(D)

Figure 4- 4 Bottom Layer IMC Forming in (A) 0h (B) 150h (C) 500h (D) 2000h Aging Time

Figure 4-4 shows the BSE pictures taken for the bottom layer of large solder joints during different aging times. The IMC layers at bottom side get thicker during increasing aging time. The shape of the IMC goes from scallop-type to planer-type. Cu_6Sn_5 forms after reflowing reaction then continue to grow and gets thicker during thermal aging. Cu_3Sn forms in between Cu_6Sn_5 and Cu substrate after certain aging time.

Chapter 5

Discussion

5.1 Growth Mechanism of IMC In Cu/IMC Interface

During the solid state aging process, what happened at the Cu/solder interface is basically Cu diffuse from substrate to Sn solder, meet the Sn atoms at the interface, forming IMC layer. If the Ni layer was added between the substrate and solder, Cu atoms need to diffuse through the Ni layer and meet Sn at the interface of Ni/Sn. Figure.5-1 is the schematic diagram shows the reactions happen between Cu substrate and SAC solder.

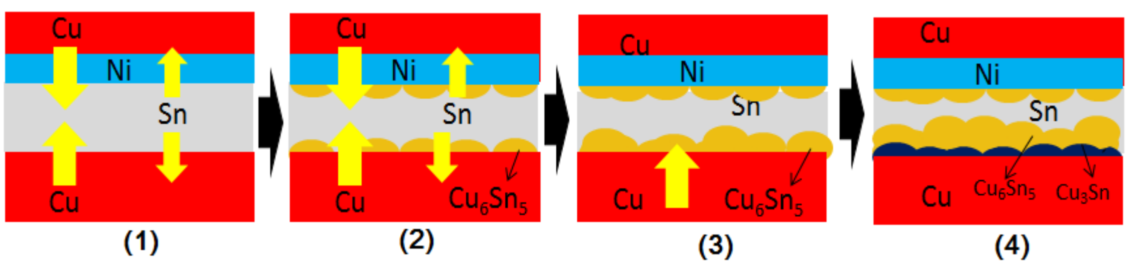


Figure 5- 1 Reaction Between Cu/Sn-based Solder in Solid State Aging.

Figure 5-1 (1) shows the structure of solder before aging (IMC formed in reflow process is ignored temporarily for the convenience). As aging time increased, at early period of solid state aging, a thin layer of Cu_6Sn_5 can be detected at the interface of Cu/Sn. The thickness of

Cu_6Sn_5 continue to increase as the aging time increase, in the bottom interface without Ni barrier, the thickness of Cu_6Sn_5 is larger than the one formed near the Ni barrier. After long enough aging time, the Cu_3Sn can be found at the interface of Cu_6Sn_5 and Cu in the bottom IMC layer. No Cu_3Sn can be found in the top IMC layer.

The thickness of Cu_6Sn_5 in both large and small solder joint was measured. The relationship between Cu_6Sn_5 thickness and aging time is showing by Figure 5-2.

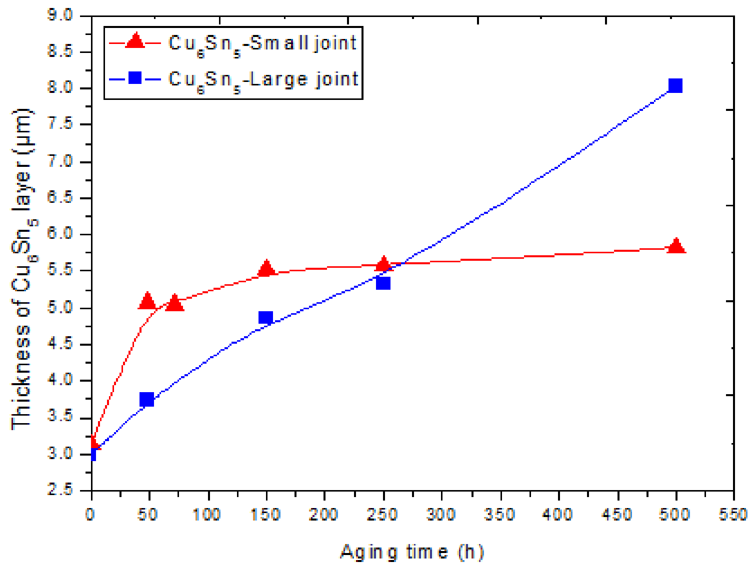


Figure 5- 2 Cu_6Sn_5 Growth Curve with Aging Time in Large and Small Solder Joint

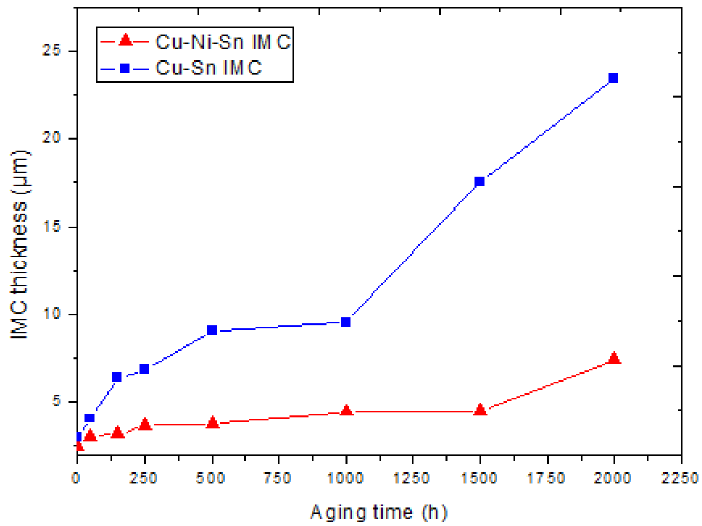
As showing by Figure 5-2, in the early aging time, Cu6Sn5 in small bump growth faster than large bump, while after 250hrs, the thickness of

Cu_6Sn_5 in large bump becomes larger than in small bump. The possible reason why small bump has a larger growth rate at the early stage can be these: In the reflowing process, when molten solder get contact with Cu substrate, Cu begin to diffuse into molten solder due to chemical potential gradient between the solder and substrate. As the stand-off height of small solder is 12.5μm, while in large solder the stand-off height is above 343μm, there is a huge size different two solder. It takes a much shorter time for a solder to be saturated with the dissolved Cu in the small solder than in large solder. The solder which is saturated with Cu, can provide a larger flux of Cu to be used in the IMC growth at Cu/Sn interface. Besides, different with the under-saturated solder, the saturated solder will not dissolve the IMC at the interface away. As the stand-off height of small solder is 12.5μm, while in large solder the stand-off height is above 343μm, there is a huge size different two solder. It is very possible that the small bump has been saturated by Cu while large bump haven't. So at the early period of solid state aging, the growth rate of IMC is larger in small bump than in large bump.

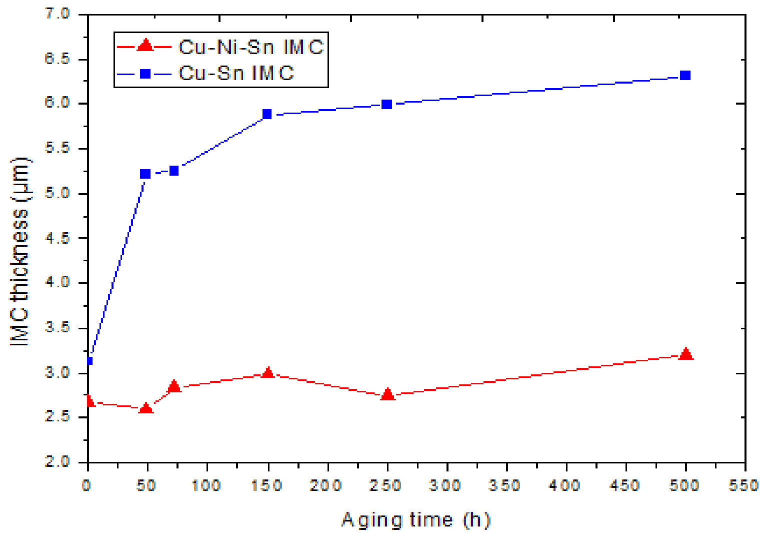
As the aging time increased, our result shows the large bump growth faster than small bump. It may due to the exhausting of Sn in the small bump.

5.2 Growth Mechanism of IMC in Ni/IMC Interface

In both large and small solder, the top side structure is Cu/Ni/Sn which is different from the bottom side Sn/Cu structure. Figure 5-3 shows the obvious impact of Ni layer on the top side IMC growth. As we can see, in case of both large and small solder joint, Sn/Cu IMC growth much faster than Sn/Ni/Cu IMC, which means Ni layer act as a very effective barrier that prevents the formation of Cu-Sn IMC. The reason why Ni can inhibit Cu-Sn IMC formation are: Ni has a very slow Sn-Ni intermetallic growth rate, and Ni layer can inhibits Sn diffusion and Cu-Sn IMC formation, furthermore, Ni_3Sn_4 can replace Cu-Sn IMC so that decrease the CU-Sn IMC growth rate and improve the reliability of solder joint.



(a)



(b)

Figure 5- 3 Cu/Ni/Sn IMC and Cu/Sn IMC Growth Curve with Aging Time in (A) Large Solder and (B) Small Solder

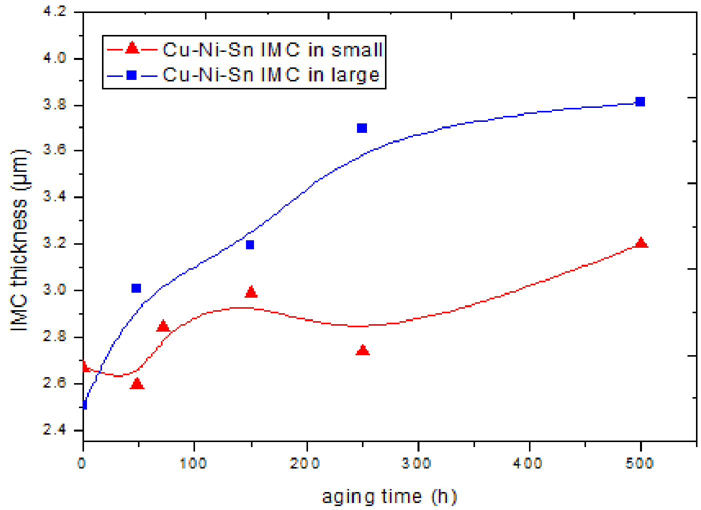


Figure 5- 4 Cu/Ni/Sn IMC Growth Curve of Small and Large Solder Joint with Aging Time

When compare the thickness of Cu/Ni/Sn top IMC layer in small and large solder joint, as showing in Figure 5-4, at the very beginning, the top layer thickness of small bump is 2.670μm, the thickness of large bump is 2.503μm, which is pretty similar with the small bump. However as the aging time increases, the Cu/Ni/Sn IMC layer in large bump growth much faster than in small bump. At 500 aging time, the thickness of the IMC in large bump come to 3.81μm; while in the small bump only 3.2μm. This result can not been explained by the thickness different of Ni barrier between large and small bump because large bump has a thicker Ni barrier which is around 8μm, while in small bump, Ni barrier is around 2μm.

A thicker Ni barrier should be more effective to avoid Cu diffusion and lead to slower IMC growth rate.

One possible explanation for this result is related to the Cu saturation in the reflow period. In the small bump, as we mentioned before, Cu get saturated much faster than in large bump. In aging period, as temperature decrease from reflowing temperature, Cu gets supersaturated in solder alloy. Both top and bottom IMC growth comparably fast. However, in bottom area, without Ni barrier, Cu/Sn IMC growth much faster than Cu/Ni/Sn IMC in top area. Cu atoms in the solder are absorbed by fast growth Cu6Sn5, after certain aging time, Cu near top area becomes unsaturated result in Cu/Ni/Sn IMC dissolution. While in large solder joint, as top area and bottom area are comparably far away from each other, the IMC growth in bottom layer will not impact Cu concentration in top layer. It's possible that Cu in the solder alloy gets saturated after reflow process, Cu/Ni/Sn IMC grows neither significant Cu concentration decrease nor IMC dissolution. So Cu/Ni/Sn IMC growth in large solder joint can grows faster than in the small joint.

5.3 Total Growth of IMC in Large and Small Solder Joint

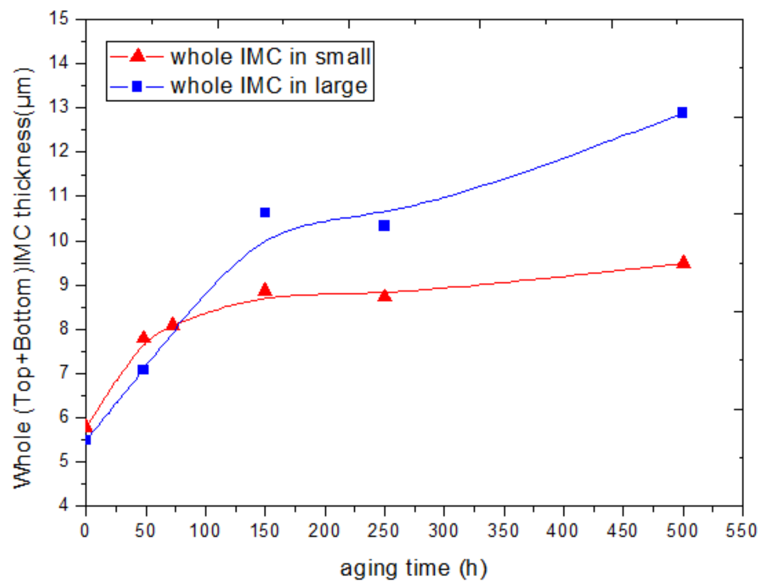


Figure 5- 5 Whole IMC Growth Curve of Small and Large Solder Joints with Aging Time.

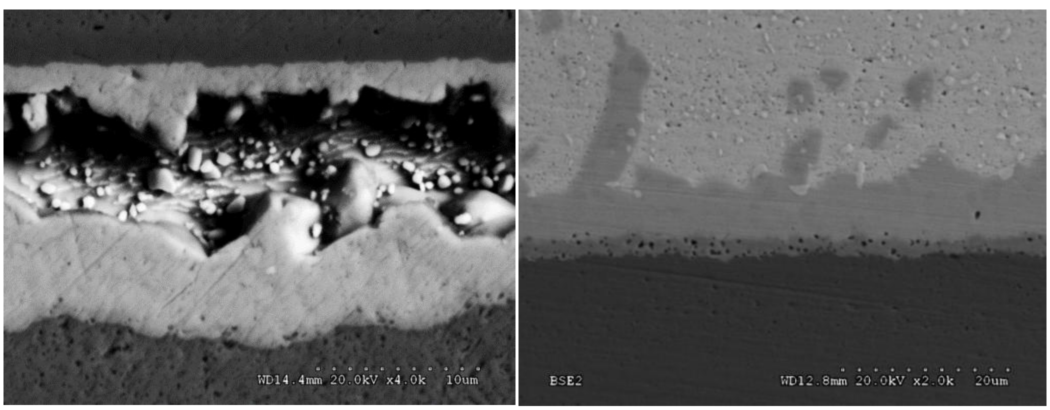
Figure 5-5 shows the comparison of whole IMC thickness between small and large solder joint. As we can see at early aging stage, the whole IMC thickness in small bump is larger than large bump, then its growth rate decreases and thickness becomes smaller comparing to large bump. The explanation of these can be: In reflowing process, it takes much shorter time for Cu to get saturated in molten solder alloy. So in the early stage, Cu flux in small solder is much higher than in large solder. Higher Cu flux result in faster IMC growth rate. While as the aging time increasing, in small solder joint, the IMC growth in top layer was negatively impact by

IMC growth in bottom layer, never the less, Sn get exhausted much faster as the small amount of storage at the very beginning.

Although the IMC thickness in small solder joint is thinner compares to large bump in long aging time, the ratio of IMC thickness with solder height is larger and results in a more dramatic microstructural change in small solder joint. So the impact of IMC thickness on the solder reliability is more seriously in small solder joint.

5.4 Kirkendall Void Formation

Figure 5-6 shows the significant kirkendall void volume different between small and large solder joint after 500h aging time.



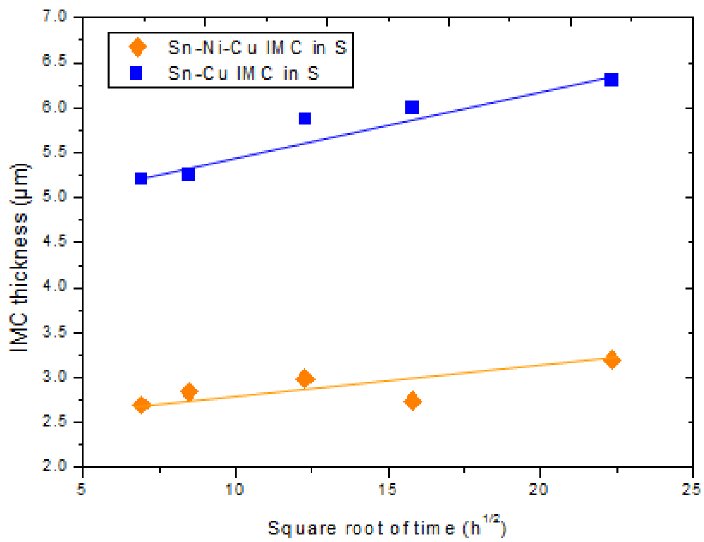
(b)

Figure 5- 6 Kirkendall Void Formation in (A) Small Solder Joint and (B) Large Solder Joint after 500h Aging Time.

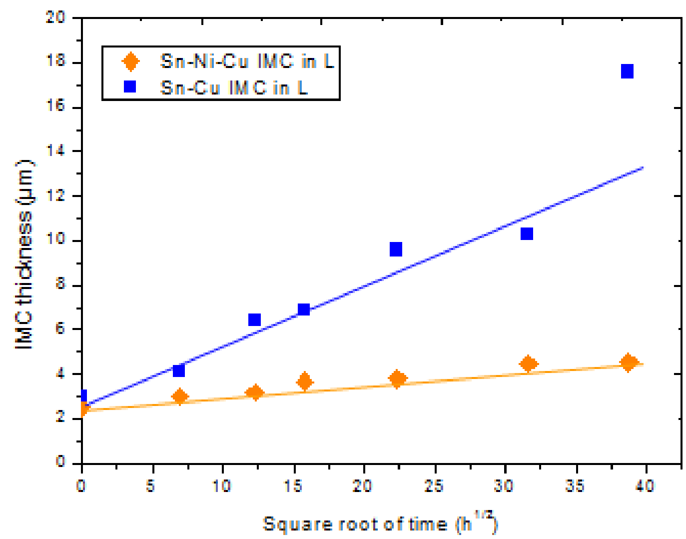
The kirkendall void forming in solid state aging is caused by the difference between the diffusion rate of Cu and Sn. The diffusion flux of Cu is higher than that of Sn in Cu_3Sn phase, so that the excess vacancies would generate behind the Cu_3Sn phase [32-34]. During same aging time, as showed by Figure 5-7, there are less amount of Cu_3Sn forming in small solder joint, so the difference between Cu and Sn flux is smaller, thus, the kirkendall void volume is smaller.

Additionally, some researchers have pointed out that kirkendall void may not be the only void type forming in the Cu_3Sn area. The formation of the void may also related to the impurities in the solder and Cu substrate. So the impurity different may also be a reason why void volume is significantly different between small and large solder joint.

5.5 Growth Kinetics of IMC in Large and Small Solder Joint



(a)



(b)

Figure 5- 7 Cu/Sn IMC and Cu/Ni/Sn IMC Growth Thickness With Square Root of Aging Time.

Figure 5-7 shows the curve of IMC thickness changing with square root of time. For small solder bump: Sn-Ni-Cu: $n \approx 0.5$; A=0.025, Sn-Cu: $n \approx 0.5$; A1=0.300; A2=0.07, means the growth of small solder bump is diffusion controlled. For large solder bump: Sn-Ni-Cu: $n \approx 0.5$; A=0.076, Sn-Cu: $n \approx 0.5$; A=0.245, means the growth of small solder bump is diffusion controlled.

5.6 Growth Mechanism of Cu_3Sn (Future Works)

The Cu_3Sn growth curve with aging time of small and large solder joint is shown in Figure 5-8. The thickness of Cu_3Sn in large solder joint is much bigger than that in small solder joint. What is the major reason of the thickness different should be study in the future works.

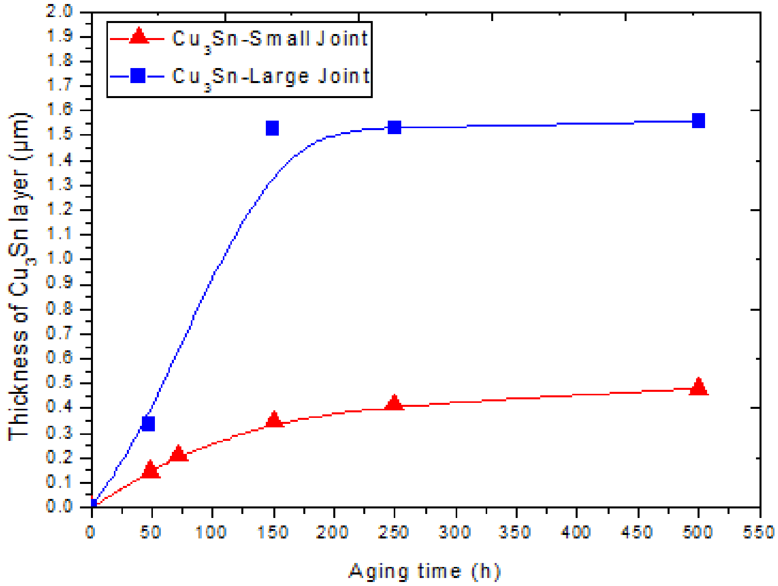


Figure 5- 8 Growth Curves of Cu3Sn in Large and Small Solder Joint.

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Biographical Information

Huandi Gu was born in Nei Mongel province, China. She got her B.S. degree in China University of Geosciences in 2010. She start her master program in Materials Science and Engineering in University of Texas at Arlington from 2012. She was working as a research assistant in Dr. Choong-un Kim’s group. During her master education, she was a member of SRC. She also served as a volunteer for summer camps in 2013 and 2014. Her research field was related to the interfacial reactions in electronic lead-free solder joint. As a master graduate student, she is able to analyze different microstructures by using different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and transmission electron microscopy (TEM).