**Effect of the degree of supercooling on growth mechanism of Cu₆Sn₅ in Pure Sn/Cu
solder joint**

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Abstract:

The growth mechanism of Cu₆Sn₅ intermetallic compound (IMC) at Sn/Cu interface reflowed under 250 °C, 275 °C, and 300 °C for a duration of 60s and undergoing highly pressurized air action(HP), water cooling(WC), air cooling(AC) or furnace cooling(FC) in the aftermath has been outlined. In addition, synchrotron radiation imaging technique has been utilized to in-situ observe interfacial Cu₆Sn₅ grains growth. It has been revealed that the morphologies of Cu₆Sn₅ grains under HP and AC are both scallop-like, whereas the samples processed with HP and FC bear plane structure and prismatic morphologies. These revelations indicate the secondary growth of Cu₆Sn₅ grains during the cooling stage as the significant determinant of the final IMC morphology. Thus, continuous growth on the rough surface (M1), spiral dislocation growth (M2), and 2D nucleation and growth (M3), have been proposed to explain the

observed morphologies of interfacial Cu_6Sn_5 grains. M1 has been recognized as the principal mechanism responsible for IMC morphology undergoing water cooling, whereas combination of M1 and M2 decide the morphological feature of interface resulting from air cooling. Finally, all of the three mechanisms (M1, M2 and M3) account for the IMC morphology corresponding to furnace cooling. As all of these three growth mechanisms are affected by the degree of supercooling (ΔT), it is inferred that the ΔT can influence the secondary nucleation of IMC at the cooling stage. With the fact that the homogeneous nucleation occurs at larger ΔT , and the relative favorability for heterogeneous nucleation at smaller ΔT ; the growth mechanisms can be mapped with the degree of undercooling. Consequently, the IMC growth mechanisms proposed and their association with ΔT , can be used to obtain an appropriate thickness and morphology of IMC to improve the reliability of solder joints.

Keywords: Solder joint, Cu_6Sn_5 grains, growth mechanism, the degree of supercooling, synchrotron radiation

1. Introduction

With the popularization of the waste electrical and electronic equipment (WEEE) and restriction of hazardous substances (ROHS) instructions, tin-based lead-free solder alloys have been widely used in modern electronic package technology. In the 3D electronic packaging, the electronic devices and the whole system is connected by soldering, and the intermetallic compound (IMC---including Cu_6Sn_5 and Cu_3Sn) formed at liquid-solid soldering interface is key factor[1-4]. Because this region is responsible for providing electrical as well as mechanical connection between devices and the whole system, shapes, sizes and distribution of IMC are crucial to the reliability of solder joints. Numerous studies showed that the IMC of soldering joints was an important factor affecting the reliability of the joint [5-7]. Due to the inherent brittleness of intermetallic compound, the interfacial IMC layer type, distribution of elements

and the non-uniformity of the coefficient of thermal expansion along the region imposing some problems, such as stress and thermal shock cracking, fatigue performance degradation significantly affect lead-free solder interconnect reliability[8-10], so the morphology, size, distribution, heterogeneity of the IMC grains will inevitably affect the reliability of solder joints and packaging. Yang [11] found that prismatic grain had a strong inhibition effect on dislocation motion and crack propagation and the crack was more difficulties to split protruding prismatic grains than to extend on the scallop-shaped grains, when the crack needed to extend. Thus, the prismatic grains joints have greater shear strength than scallop grains. As the increment of soldering temperature, IMC thickness increases and the shear strength also continues to decline. Meanwhile, lee [12] also found that the tensile strength declined with the roughness and thickness of IMC increased, and the stress distribution of Sn-Ag/Cu soldering joint by using FEM simulation found that stress centralization in the solder/Cu₆Sn₅ interface was easy to induce the formation and growth of crack. The cracks appeared in the solder/Cu₆Sn₅ interface and propagated along the interface when the IMC thickness was less than 1μm. While the thickness of IMC was 1 ~ 10μm, cracks appeared near the prominent Cu₆Sn₅ waist then toward with the solder/Cu₆Sn₅ interface with the direction of approximately 45° extending into the solder, ultimately forms dimple fracture morphology. When the IMC thickness exceeded 10μm, solder/Cu interface became rough and was accompanied with the residual stress which caused by the transformation of the crack produced and extended in the Cu₆Sn₅ layer. As for the electronic packaging soldering process, the reflow soldering time is very short (<1min). So, the Cu₃Sn IMC formed in the interface is very thin (<1μm), which can be ignored as compared with the thickness of the Cu₆Sn₅ layer[5]. However, under thermal aging conditions, Cu₃Sn mainly relies on the consumption of Cu₆Sn₅ IMC and the Cu substrate to continuously grow up to a thickness of tens of microns. The Cu₆Sn₅ layer formed during reflow soldering not only supplied material and nucleation

67 sites for Cu_3Sn growth, but also made the Sn atoms in the solder matrix difficultly diffuse to the
68 $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ reaction interface. At the same time, the dissolved Cu atoms from Cu substrate
69 continuously diffused into the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ reaction layer, which leads to the enrichment of the Cu atom
70 concentration in the reaction layer and promotes the reaction of Cu_6Sn_5 and Cu atoms to form Cu_3Sn .
71 Due to the inherent brittleness of Cu_3Sn IMC and IMC/Cu thermal expansion coefficient not matched
72 [13], the growth of the hard and brittle Cu_3Sn layer would induce the formation of Kirkendall voids, and
73 the voids are the source of cracks. As the Cu_3Sn IMC continuous growth, more voids are formed. When
74 the soldering joint is stressed, the stress will form a stress concentration zone at the void, and the crack
75 at the void will preferentially expand again and extend to the interface. As a result, the fracture position
76 changed from the solder matrix to the solder/ Cu_6Sn_5 interface, even $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ interface and Cu_3Sn
77 layer. What's more, the fracture also changed from quasi-cleavage (toughness) to brittle fracture [14-16],
78 and the mechanical properties of the joint continue to decrease accordingly. But for reflow soldering, the
79 soldering reaction production (IMC) mainly grew into the liquid Sn solder matrix, and the concentration
80 of Sn atoms at the soldering interface is much higher than Cu atoms. Besides, the growth activation
81 energy of Cu_3Sn (85.51kJ/mol [17]) is higher than Cu_6Sn_5 (14.91kJ/mol [17]), and Cu_3Sn is more stable
82 under low aging temperature ($<190^\circ\text{C}$) while Cu_6Sn_5 is more stable with high reflow soldering
83 temperature ($>200^\circ\text{C}$)[17-19]. Consequently, Sn atoms and Cu atoms react mainly to form Cu_6Sn_5 IMC
84 during reflow soldering. Through the analysis of research results by above-mentioned literature, it should
85 be clear that the temperature/cooling method combination during reflow soldering process has a
86 significant impact on the morphology and thickness of Cu_6Sn_5 , which will also should have a certain
87 impact on the subsequent growth of Cu_3Sn IMC (Such as, whether the evolution time of scallop-shaped
88 IMC into Cu_3Sn is faster than prismatic IMC, and prismatic IMC is last longer and have better stability

during thermal aging and cycling? Moreover, whether the thickness of the Cu_6Sn_5 layer formed during reflow soldering has an effect on the subsequent growth of Cu_3Sn IMC, etc. So, the related reasons and mechanisms will need to be studied in the future). As all well known, reflow soldering is a necessary prerequisite for the aging service of soldering joint. Therefore, it is necessary to clearly study the growth mechanism and non-uniform distribution of liquid/solid interface Cu_6Sn_5 IMC grains during reflow soldering, which will help improve the interface reliability of soldering joints in electronic packaging.

Though several grain growth models of solid-liquid interfacial Cu_6Sn_5 IMC based on certain assumptions have been built, a uniform and extensively recognized model has not been formed at present. Among them, there are two representative models, namely, Tu's diffusion controlled growth model of scallop-like Cu_6Sn_5 grains accompanied by a ripening reaction [5] and Shaefer's grain boundary diffusion control model [20]. In Tu's model [5], it is assumed that the influence of Cu_3Sn phase on copper diffusion was ignored, and the Cu atoms could diffuse into the molten solder through a thin Cu_6Sn_5 layer and the liquid channels between adjacent scallop-like Cu_6Sn_5 grains. In addition, Cu_6Sn_5 grain was assumed to be a hemisphere, and Gibbs-Thomson effect has been used to formulate the expression for the Cu concentration in the molten solder at the surface of the grain. Owing to the difference in radius of curvature, the concentration gradient formed between adjacent grains led to the larger grains growing up and the small ones becoming shrink and disappear. Under the Gibbs-Thomson effect, the size of scallop-like Cu_6Sn_5 grew larger but number being fewer with the extent of soldering time. Finally, the time dependence of layer thickness or grain size being $1/3$ was obtain, namely, this diffusion control model was driven basically by ripening flux for the growth of Cu_6Sn_5 grains. As for Schaefer's model [20], the influence of thin Cu_3Sn layer on the diffusion of Cu and Sn atoms was also neglected, which was similar to Tu's model. Meantime, this model also assumed the scallop-like Cu_6Sn_5 grains having a hexagonal

shaped base towards Cu substrate and a rounded top in contact with liquid solder, and these grains were thought to become equiaxed as they grew. Liquid solder is considered to approach saturation with Cu during the initial stage. It has been stated that the free diffusion of Sn with lower melting temperature, rather than Cu, largely controls the growth of layer thickness. Because uniform grain size assumed, it has been deduced theoretically that the grain boundary diffusion is the predominant mechanism for atoms transport through the layer. In addition, the curvature of Cu_6Sn_5 grains does not bring any effect on the interfacial components of Cu_6Sn_5 phase because the grain boundary diffusion is governing. The time dependence of layer thickness or grain size being $1/3$ is also consistent with flux driven ripening model of Tu et al [5].

However, there are two limitations for above two models. Firstly, the effect of Cu_3Sn layers between Cu and Cu_6Sn_5 on the growth of Cu_6Sn_5 grain size and thickness is neglected in above two models. Secondly, interfacial Cu_6Sn_5 grains are not all scalloped or hexagonal shape with a rounded top, because the faceted morphology of Cu_6Sn_5 grains formed is also found during the soldering process[21]. Facet morphology of Cu_6Sn_5 grains is remarkably different from scalloped or hexagonal one, and their growth behaviors can't be reasonably explained by Tu's or Sheacher's models.

The growth process of interfacial IMC grain belongs crystal growth category and is in accordance with nucleation, growth and other basic theories of crystal growth. For the study of traditional crystal growth theories, there are a few widely used interface structural models, such as Frank spiral dislocation model[22-25], Jackson double atomic layer model[26], diffusion interface model (Temkin multi-layer interface model)[27], the continuum model (Cahn model)[28] and W.Kossel model[29], which can explain interface structures during crystal growth in vapor, solution and melt phases. The growth of liquid-solid interfacial IMC grain occurs in molten solder, and this phenomenon can be considered

similar to the crystal growth in solutions. Thus, the first four models are governed by this consideration as following. (1) In Frank spiral dislocation model, the outcrop of spiral dislocation is a source for the growth of nucleation point, and the grains in accordance with the spiral dislocation arrangement are around the outcrop of the spiral dislocation to grow. The outcrop of spiral dislocation is regarded as a crystal growth step source, which successfully explains the phenomenon that crystals can grow at very low supersaturation. (2) The Jacksonian double atoms model (Jackson model), which only considers the two-layers interaction on the crystal phase. The equilibrium structure of the interface is analyzed according to the value of the interfacial phase change entropy factor at the solid-liquid interface. Therefore, the interface phase change entropy is proposed, also known as the Jackson factor(α), to describe the roughness or smoothness of the crystal surface. $\alpha = 2$ is taken as the criterion of the equilibrium properties of various crystal materials: $\alpha < 2$ is the rough interface for crystal growth interface whereas $\alpha > 2$ is the smooth interface for crystal growth interface. Thus, the Jackson factor(α) can be calculated to predict the roughness of the crystal growth interface. (3) The diffusion interface model (Temkin multi-layers interface model) can be used to determine the number of interface layers in thermal equilibrium state, and then the influence of the interface phase change entropy on the interfacial structure is also obtained according to the Gibbs free energy change in the non-equilibrium state. But this model ignores the atomic segregation effect. In this model, it is also concluded that the effect of phase change entropy on the interfacial structure in the supercooled state. Namely, when the degree of supercooling exists, the interface will transform from smooth interface into rough interface which facilitates crystal growth. (4) The continuum model (Cahn model) gives the range of growth driving force for dislocation growth mechanism and the normal growth mechanism, and also predicts the relationship between the crystal growth mechanism and the degree of supercooling. When the degree of supercooling is large, the

continuous growth controls crystal growth; But in terms of very small degree of supercooling, crystal growth is controlled by the spiral dislocation growth. However, the growth behavior of interfacial IMC grain in Sn/Cu soldering joint has its disparate features as compared with solutions. Firstly, the solid interface is in a dynamic process since Cu substrate is dissolving and the IMC layer is getting thicker with time during soldering progress. Secondly, the dissolution of Cu substrate leads to the change of Cu concentration in liquid solder. Therefore, it is hard to explain the growth behavior of interfacial IMC by simply adopting any one of the above models in soldering process. The growth behavior of Cu_6Sn_5 grains with small plane and prismatic top during the cooling stage cannot be explained by any existing interfacial IMC grain growth theories in Sn/Cu solder joints.

In summary, the growth mechanism of IMC grain at Sn/Cu interface needs to be further study. Hence, in this paper, the growth behavior of interfacial Cu_6Sn_5 grain by different cooling rates in Sn/Cu solder joints have been studied. In addition, synchrotron radiation real-time imaging technology is also applied to in-situ observe the growth of interfacial IMC grain in Sn/Cu solder joint. Considering the four classic crystal growth models (Frank spiral dislocation model, Jackson model, Temkin multi-layers interface model, Cahn model), new mechanisms are proposed to explain the different IMC morphologies formed (such as, scallop with plane structure and prismatic top) under different cooling conditions. It is also expected that new mechanisms proposed can make people widely known and accurate description of the growth behavior of interfacial IMC, and finally providing theoretical support to improve the reliability of the solder joint.

2. EXPERIMENT METHOD

The Pure Sn (Dalian Golden Saddle Welding Limited Company, China; purity: 99.99%, Melting point: 231.89 °C) solder with a diameter of 1mm solder ball is used to react with polycrystalline Cu (Qingyuan

Metal Materials Limited Company, China; purity: 99.99%, Melting point: 1083.4 °C, the size : 2000μm
 × 2000μm × 100μm) substrate in the reflow furnace at 250 °C, 275 °C, and 300 °C with reaction time
 being 1min as shown in Fig.1 (a). Then, the samples are cooled in water (727 °C.s⁻¹, WC), air (7.4 °C.s⁻¹, AC) and furnace (0.38 °C.s⁻¹, FC, as show in Fig.2). In addition, high pressure air (0.8Mpa, HP) is used
 to remove excess liquid solder (that is, for acquisition of the IMC morphology at heat preservation stage)
 as show in Fig.1 (b). The explanation of surface treatment for Cu substrate is written as: Firstly, 5vol.%
 HCL+ 95vol.% ion water solution is used to remove the oxide film on the polycrystalline Cu substrate
 with 5s in the ultrasonic shock tank, and then it is cleaned with 30s by alcohol in the ultrasonic shock
 tank. Finally, Cu substrate is dried with a blower fan to prepare for soldering. Heat preservation stage is
 the stage in this experiment in which the reflow soldering temperature is held constant for 1min. This
 stage lies between the heating and cooling stage. Two kinds of cooling samples are prepared for SEM by
 grinding, polishing, etching with 5vol.% HNO₃ + 2vol.% HCl + 93vol.% C₂H₅OH solution to reveal the
 cross-sectional morphology. Similarly, some samples were etched by 10vol.% HNO₃ solution to remove
 the solder away for top-view observation. The top-view and cross-sectional-view of IMC are observed by
 SEM. In addition, the growth of IMC at Sn/Cu liquid-solid interface under 250 °C, 275 °C, and 300 °C
 are directly observed by synchrotron radiation real-time dynamic imaging technology in Shanghai light
 source BL13W1 line station. The thickness of the solders (Pure Sn) and Cu substrate were 100μm. The
 cross-section of the Cu substrate was polished and a butt joint was made to connect it with the solder,
 having lead-free flux (AMTECH: NC-559-ASM) in between. Schematic diagrams of synchrotron
 radiation as shown in Fig. 1(c). The energy of the monochromatic beam was 18keV and a charge coupled
 device (CCD) with resolution ratios of 0.37 μm/pix was used, and the corresponding exposure time was
 3s, respectively. The samples were put into a specially designed soldering furnace with a hole through

which the formation and evolution of interfacial IMC grains during the soldering process could be observed by the synchrotron radiation real-time imaging technology. The specimen preparation was similar to that in the previous study[30, 31] as shown in Fig. 1(c).

Fig.1 Schematic diagrams of (a) reflow soldering sample, (b) liquid solder removed by high-pressure air and (c) configuration for synchrotron radiation experiment

Fig.2 The furnace cooling curve during the cooling stage of soldering

3. RESULTS AND DISCUSSION

3.1. The morphology evolution of interfacial Cu_6Sn_5 grain

According to the existing theories for IMC growth[5,20], higher soldering temperature or longer soldering time leads to a larger size of Cu_6Sn_5 . In order to reduce factors affecting grain size, the same soldering time (1min) was used in this paper. At each temperature, the cooling condition was changed to study its influence on the morphology of Cu_6Sn_5 grain. Fig.3 is the top-view SEM images of the

morphologies of Cu_6Sn_5 grains formed under various temperature with 60s by high-pressure air, water cooling, air cooling, and furnace cooling respectively. The morphology of Cu_6Sn_5 obtained by using high pressure air is regarded as the final morphology of Cu_6Sn_5 at the heat preservation stage[32]. During the heat preservation stage, the morphology of Cu_6Sn_5 is all scallop-like under different soldering temperature as shown in Fig.3(a, e, i). For water cooling condition, the Cu_6Sn_5 grains have a shape of scallop-like with a few small planes on the surface. With the temperature increasing, the IMC grains and small plane both grow bigger as shown in Fig.3(b, f, j). When the cooling condition is air cooling, the morphology of Cu_6Sn_5 grain observed is the scallop-like with a small plane top at 250 °C and the morphology of Cu_6Sn_5 is scalloped with a plane structure top at 275 °C and 300 °C as shown in Fig.3(c, g, k). With the increment of temperature, the plane structure grows much wider. Comparing with water cooling and air cooling, the morphology of Cu_6Sn_5 under furnace cooling is obviously different. From 250°C to 300°C, the morphology of Cu_6Sn_5 is scallop-like with a prismatic top and the prismatic becomes much coarser and longer as shown in Fig.3(d, h, l).

Fig.3 SEM images of top -view of Cu_6Sn_5 and the soldering time is 1min. (a. 523K (250°C) high-pressure air, b. 523K (250°C) water cooling, c. 523K (250°C) air cooling, d. 523K (250°C) furnace cooling, e. 548K (275°C) high-pressure air, f. 548K (275°C) water cooling, g. 548K (275°C) air cooling, h. 548K (275°C) furnace cooling, i. 573K (300°C) high-pressure air, j. 573K (300°C) water cooling, k. 573K (300°C) air cooling, l. 573K (300°C) furnace cooling).

cooling, e. 548K (275°C) high-pressure air, f. 548K (275°C) water cooling, g. 548K (275°C) air

cooling, h. 548K (275°C) furnace cooling, i. 573K (300°C) high-pressure air, j. 573K (300°C) water

cooling, k. 573K (300°C) air cooling, l. 573K (300°C) furnace cooling

Fig.4 represents the cross-section SEM images of the morphologies of Cu_6Sn_5 grains formed under various temperature with 60s by high-pressure air, water cooling, air cooling, and furnace cooling respectively. From 250 °C to 300 °C, the morphology of Cu_6Sn_5 is observed to be scallop-like under high-pressure air (Fig.4(a, e, i)), and the morphology is scallop-like with few small planes on the surface under water cooling as shown in Fig.4(b, f, j). For air cooling condition, it is more obvious to see that the morphology of Cu_6Sn_5 grains is scallop-like with a plane structure top in Fig.4(c, g, k). It should be also noted that the Cu_6Sn_5 grains are scallop-like with a prismatic top under furnace cooling as shown in Fig.4(d, h, l). With soldering temperature increasing, the thickness of IMC layers and grains both become thicker and coarser. In the meantime, it is also found that the plane structure and prismatic Cu_6Sn_5 grains with Cu substrate have an angle from 30 ° to 60 °, which is highly similar with Yang's study[33].

Fig.4 SEM images of cross-section of Cu_6Sn_5 and the soldering time is 1min. (a. 523K (250°C) high-pressure air, b. 523K (250°C) water cooling, c. 523K (250°C) air cooling, d. 523K (250°C) furnace cooling, e. 548K (275°C) high-pressure air, f. 548K (275°C) water cooling, g. 548K (275°C) air cooling, h. 548K (275°C) furnace cooling, i. 573K (300°C) high-pressure air, j. 573K (300°C) water

cooling, k. 573K (300°C) air cooling, l. 573K (300°C) furnace cooling

As we known, the high-pressure air removing liquid solder experiment is equivalent to the heat preservation stage of soldering[32]. Considering Fig.3 and Fig.4, we obtain that the morphology of Cu_6Sn_5 grains at the heat preservation stage and water cooling are both scallop-like, which can be well explained by the models of FDR[5] and Schaefer[20]. But for air cooling and furnace cooling, the top morphologies of Cu_6Sn_5 grains are plane structure and prismatic, which can't be reasonably explained by the existing models of interfacial IMC. It should also be noted that the cooling stage of soldering has a significant influence on the Cu_6Sn_5 growth and then makes the morphology transformation of IMC grain. The result is highly consistent with Yang[34] and mine[21] previous studies. In order to in-situ verify the effect of the cooling stage on the morphology transformation, synchrotron radiation real-time imaging technology is applied to in-situ observe the interfacial IMC growth in Sn/Cu solder joints with the soldering time of 60 min at 250 °C, 275 °C, and 300 °C as shown in Fig.5. It is observed that the morphology of Cu_6Sn_5 grains is scallop-like with a round top at the heat preservation stage, and the morphology of Cu_6Sn_5 grains transform from scallop-like with a round top to scallop-like with a tip-top at the subsequent cooling stage. These results are good march with the above phenomenon as shown in Fig.3 and Fig.4. Therefore, it can be confirmed that the cooling stage obviously affects the IMC morphology transformation by the Cu_6Sn_5 precipitation from solder to promote IMC growth at the cooling stage or solidification, namely, the secondary growth of IMC grain.

Fig.5 The synchrotron radiation images of Sn/Cu joints at 523K, 548K, and 573K (250°C, 275°C and 300°C) with 60min. (a₁~c₁) and (a₂~c₂) are the end of heat preservation and furnace cooling during soldering.

3.2. Assumptions

On the basis of the existing theories and researches, the following deductions will be used for this new model proposed: (1) The surface of Cu substrate is rough in the atomic scale. (2) Cu atoms diffuse from the surface of solid Cu substrate to the liquid solders [35,36]. Due to concentration gradient effect, interfacial Cu atoms continuously dissolve into solders and Cu concentration in liquid solders firstly reaches saturation at the interface. (3) According to the Cu-Sn binary equilibrium phase diagram, when Cu atoms interact with the liquid solder (Sn), Cu₆Sn₅ phase forms by the reaction of Sn and Cu atoms which is particle-like and distributed at Sn/Cu interface. When the Cu concentration at the solder/substrate is supersaturation, Cu and Sn atoms will precipitate to form Cu₆Sn₅ phase at the interface.

The underlying assumptions for this new model include:

- The growth of Cu₆Sn₅ at the solid-liquid interface belongs to the category of crystal growth.
- The surface of Cu₆Sn₅ phase formed during soldering is rough.
- The Cu₆Sn₅ phase grows up by means of heterogeneous nucleation. The favorable nucleation site for the subsequent growth of Cu₆Sn₅ is at the surface of primary grains.
- Cu substrate does not dissolve anymore at the Cu₆Sn₅ nucleation sites of Cu substrate, but at other sites, it will still dissolve into liquid solder. Cu atoms are driven by Kirkendall Effect and body diffusion from Cu substrate diffuses through Cu₆Sn₅ grains into liquid solder.
- The growth of Cu₆Sn₅ grain is controlled by the mechanisms of continuous growth on the rough surface, spiral dislocation growth, and two-dimensional nucleation and growth.

- The Cu_3Sn (ϵ -phase) layer is planar and very thinner (especially grain boundaries areas), and its morphology and thickness have not significantly changed in the soldering progress, even for a long soldering time[5,20,21,32,36]. In addition, the liquid solder matrix directly connects with Cu substrate by the liquid channels [36]. The grain boundary diffusion controls the Cu_6Sn_5 growth by Schafer's theory[20]. So, in this model, it is assumed that the Cu_3Sn (ϵ -phase) is not a barrier layer for Sn and Cu atoms free diffusion and can be neglected[5].

3.3. Effect of the degree of supercooling on nucleation of the secondary growth for interfacial Cu_6Sn_5 grain during the cooling stage

According to the heterogeneous nucleation theory[37], the nucleation at the interface is easier than homogeneous nucleation because existing interface and defects contribute to a part of the surface energy needed for nucleation. The expression for heterogeneous nucleation and homogeneous nucleation can be written as(1), (2) and (3).

$$\Delta G_{\text{het}} = \Delta G_{\text{hom}} f(\theta) \quad (1)$$

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4} \quad (2)$$

$$\Delta G_{\text{hom}} = \frac{16\pi\sigma^3 T_m^2}{3(H_m \bullet \Delta T)^2} \quad (3)$$

Where ΔG_{het} is nucleation energy for heterogeneous nucleation. σ is the energy of the new interface, T_m is the melting point, H_m is the heat of fusion, ΔT is the degree of supercooling and θ is the wetting angle between the liquid phase and the heterogeneous nucleation substrate. ΔG_{hom} is nucleation energy for homogeneous nucleation.

As the wetting angle between the liquid solder and Cu substrate is less than 180° during the soldering process, the value of $f(\theta)$ is less than 1 and the value of ΔG_{het} is thus less than that of ΔG_{hom} . Therefore,

heterogeneous nucleation is easier than homogeneous nucleation in the thermodynamically. At the cooling stage of the soldering process, there exists a secondary growth of Cu_6Sn_5 grains in Fig.3 and Fig.5. Because the primary growth of Cu_6Sn_5 grains appears rough surface at the heat preservation stage as shown in Fig.3(a, e, i), the contact area between Cu_6Sn_5 grain and liquid solder will be bigger than that with the smooth surface. So, it not only contributes to the dissolution of Cu_6Sn_5 into liquid solders but also provides a favorable position for the nucleation of Cu_6Sn_5 . Consequently, Cu_6Sn_5 grains formed at the early stage are more rugged and offer favorable surfaces for the heterogeneous nucleation to form subsequent Cu_6Sn_5 grains. As we know from Eq.3, the degree of supercooling affects the nucleation energy. When the degree of supercooling is sufficiently big, the homogeneous nucleation energy will very small and then the homogeneous nucleation can easily occur, namely, two-dimensional nucleation and growth as shown in Fig.3(e). But for the small degree of supercooling, the heterogeneous nucleation is easier than homogeneous nucleation, such as the continuous growth on the rough surface and spiral dislocation growth in Fig.3(i, k, l).

To be conclusion, the degree of supercooling play a significant role on the nucleation of secondary growth for interfacial Cu_6Sn_5 grains during the cooling stage of soldering.

3.4. Analysis of growth mechanism and kinetics of interfacial Cu_6Sn_5 grain during the cooling stage in Sn/Cu solder joints

According to the research by Yang[38] and Jackson[26], the surface of scalloped Cu_6Sn_5 grains at the liquid/solid interface is rough. Because continuous growth on rough surface mechanism has little effect on the morphology of Cu_6Sn_5 grains, the interfacial Cu_6Sn_5 remains scallop-like under this mechanism. With time prolonging and temperature reducing, Cu and Sn atoms in the liquid solder near the liquid/solid interface precipitate on the existing Cu_6Sn_5 grains and then promote the secondly growth

of Cu₆Sn₅. Due to the incompleteness of the actual crystal, there are a large number of supersaturated vacancies in the primary crystal surface. So, Cu and Sn atoms tend to accumulate at atomic vacancy sites of the rough surface of Cu₆Sn₅ grains. Consequently, atomic accumulates into a certain extent to form a spiral dislocation, which is parallel to the dislocation line. Due to the low energy of dislocation at the crystal interface, the atoms continue to precipitate and form a spiral dislocation source at the rough surface as shown in Fig.6(a). Then, the atoms precipitate continuously at the spiral dislocation growth source, leading to the heterogeneous nucleation and spiral upward growth of Cu₆Sn₅ grains along the growth steps of spiral dislocation as shown in Fig.6. Cu₆Sn₅ has a close-packed hexagonal (HCP) structure and its unit cell structure is shown in Fig.7(a, b). Lattice constant c is bigger than lattice constant b, so atom density is less in c-axis, thereby resulting in prior growth of Cu₆Sn₅ along this axis. It is also confirmed that $\{10\bar{1}0\}$ is the Miller index family of side planes of Cu₆Sn₅ crystal in the previous studies [27,38-40], which is minimum energy plane for a close-packed hexagonal structure[41,42]. Minimum energy is needed on this plane for the growth of grains and the morphology of crystal formed is stable. Thus, the morphology of Cu₆Sn₅ is quadrangular or hexagonal prism type. Just as shown in Fig.7(c), the scallop-like Cu₆Sn₅ with a prismatic top can be described by a spiral dislocation growth mechanism.

Fig.6 Schematic diagrams of (a-f) growth process of spiral dislocation around spiral dislocation source

step by step, (a) spiral dislocation source and (b, c) the outcrop of spiral dislocation

In the meantime, naked growth steps of the spiral dislocations on the Cu_6Sn_5 crystal can be used as the steps source for two-dimensional nucleation and growth mechanism. There are some obvious veined lines observed on the side planes of Cu_6Sn_5 as shown in Fig.3(d, h, l) and Fig.7(c), which should be the result of the accumulation of multilayer steps. As the solidification process continues, Cu_6Sn_5 grains get coarsening in the width direction according to the two-dimensional nucleation and growth mechanism. Comparing with air cooling sample, it can be observed that the Cu_6Sn_5 grain under furnace cooling condition is much thicker and longer as shown in Fig.3(g, h).

Fig.7 (a) The simplified diagram of close-packed hexagonal crystal structure, (b) the structure of the Cu_6Sn_5 crystal unit cell; a , c in italics near the lines of dashes represent coordinate axis. (c) the microstructure diagram of Cu_6Sn_5 grain and SEM graph of prismatic grain.

The three growth mechanisms, namely continuous growth on the rough surface (M1), spiral dislocation growth (M2) and two-dimensional nucleation and growth (M3), are proposed to explain the phenomena that scallop-like Cu_6Sn_5 grains have a small plane and prismatic top. As for the crystals growth, the degrees of supercooling for the three growth mechanism are different. The kinetic equations (4), (5) and (6) correspond to the expressions for the degree of supercooling (ΔT_i) with continuous growth on the rough surface, spiral dislocation growth, and two-dimensional nucleation and growth respectively [43].

$$\Delta T_0 = R / K_0 \quad (4)$$

$$\Delta T_1 = (R / K_1)^{1/2} \quad (5)$$

$$\Delta T_2 = \frac{-B_2}{\ln(R / K_2)} \quad (6)$$

Wherein, K_0 , K_1 , K_2 and B_2 are kinetic coefficients for continuous growth on the rough surface, spiral dislocation growth and two-dimensional nucleation and growth respectively and R is growth rate parameter for crystal at soldering interface. For the same soldering interface, the degrees of supercooling for these three growth mechanisms are usually $\Delta T_2 > \Delta T_1 > \Delta T_0$, which indicates that the degree of

supercooling for continuous growth on rough surface is minimum, whereas is the maximum for two-dimensional nucleation and growth. Therefore, rough surface, small plane and prismatic are at the different isothermal surface at the same solid/liquid interface, and the growth of prismatic grains occur at the location of lower temperature. During the soldering process, the degree of supercooling varied along the vertical direction of the Cu substrate to liquid solder. The temperature at the liquid-solid interface is higher than the others in the liquid solder and Cu substrate during the solidification process, which leads to the temperature gradient formed among the three places[21]. Due to influence of the temperature gradient, Cu_6Sn_5 grains show different morphologies. So, Cu_6Sn_5 grains have a prismatic top related to the higher degree of supercooling at the top in Fig.3(d, g, h, k, l). As for the prismatic top, horizontal size is much smaller than the vertical size because of different growth mechanisms. The growth in vertical and horizontal direction is controlled by spiral dislocation growth and two-dimensional nucleation and growth mechanism, respectively. The growth rate in the vertical direction is higher than that in the horizontal direction because the spiral dislocation growth occurs at the lower degree of supercooling than two-dimensional nucleation and growth. Therefore, the prismatic top is observed to be long and narrow as shown in Fig.3(K).

The degrees of supercooling under water cooling, air cooling, and furnace cooling conditions are designated as ΔT_{WC} , ΔT_{AC} and ΔT_{FC} respectively. To our best knowledge of crystal growth, the bigger is the cooling rate, the bigger will be the degree of supercooling. Thus, faster cooling rate leads to a higher degree of supercooling, namely, $\Delta T_{\text{WC}} > \Delta T_{\text{AC}} > \Delta T_{\text{FC}}$.

As we know from literature[21], the relation between the small plane of Cu_6Sn_5 grains and the degree of supercooling can be expressed by the following formula.

$$S \approx 2\Delta T r / W \quad (7)$$

Where S is the area of the small plane, ΔT is the relative degree of supercooling of a small plane center with respect to the hemispherical, r is the radius of curvature of the IMC, W is the liquid/solid interface temperature gradient. In Eq.(7), since ΔT is greater than 0, IMC is the outer convex shape from the solid phase into the liquid solder at the solder interface, and the radius of curvature r is greater than 0. Thus, the necessary condition for the formation of a small plane at the interface can only depend on the positive and negative of W . Small plane is formed when the W and S are positive. Due to the big degree of supercooling, the small plane is easy to form under water cooling condition as shown in Fig.3(b, f, j). The degree of supercooling under water cooling condition is the largest among three cooling conditions, but Cu and Sn atoms could not get sufficient time to move to the location of spiral dislocation growth steps forming Cu_6Sn_5 . In addition, the nucleation rate has a great affection for the Cu_6Sn_5 growth. The nucleation rate (N) can be expressed as[44]

$$N = C \exp(-A / kT) \exp(-Q / kT) \quad (8)$$

Where C is a proportional constant, A is the nucleation work, Q is the diffusion activation energy required for atoms to cross the liquid-solid phase interface, k is Boltzmann's constant, and T is the absolute temperature (K). The value of Q varies less along with the temperature, thus, we can believe the value of Q to be a constant. When the degree of supercooling increases, the diffusion rate of atom get slow. Therefore, the value of $\exp(-Q/kT)$ becomes smaller with the degree of supercooling increasing as shown in Fig.8(a). From literature[37], we learn that the nucleation work has the relationship with the degree of supercooling as the following expression.

$$A = \frac{16\pi \sigma^3 T_m^2}{3H_m^2} \frac{1}{\Delta T^2} \quad (9)$$

Where σ is the surface free energy, H_m is the heat of fusion, T_m is melting point, ΔT is the degree of supercooling. With the degree of supercooling increasing, the A gets smaller. From Eq.(7) and Fig.8(a),

we obtain N_{max} when $A=Q$. If we let $Q=2280\text{J mol}^{-1}$ [33], $H_m=1.398\text{J g}^{-1}$ [33] and $\sigma=0.1\text{J m}^{-1}$ [44, 45], we obtain $\Delta T_{Nmax}=374.418\text{K}$ (101.418°C). Consequently, the nucleation rate under three cooling conditions can be elaborated as shown in Fig.8(b).

Fig.8 The relationship between the degree of supercooling degree and (a) $\exp(-A/kT)$, $\exp(-Q/kT)$ and (b) the nucleation rate

As we know from the experiment, the water cooling rate is up to 727°C.s^{-1} . Thus, it will lead to a very big degree of supercooling, which can be easy to form the small plane on the surface of Cu_6Sn_5 grains. But the nucleation rate can be smaller because of the bigger degree of supercooling as shown in Fig.8(b). Due to fast cooling rate for water cooling condition, there is a very short time for Cu and Sn atoms precipitating on the surface of grains to promote the two-dimensional nucleation and growth. Therefore, continuous growth on rough surface mechanism is the primary mechanism for Cu_6Sn_5 growth under this condition. Finally, the morphology formed of Cu_6Sn_5 grains under water cooling condition is still scallop-like with few small planes on the surface, which is similar to the morphology of grains at the heat preservation stage.

As for air cooling condition, the degree of supercooling (value) is between water cooling and furnace cooling. Due to the big degree of supercooling, the small plane is also easy to form under air cooling condition as shown in Fig.3(c). Meantime, the solidification time is slightly longer and Cu and Sn atoms have relatively enough time diffusing to the location of spiral dislocation and growing along c-axis in compliance with spiral dislocation growth mechanism. For this condition, there is still not enough time for the growth of Cu_6Sn_5 by the two-dimensional nucleation and growth mechanism. In addition, the growth of Cu_6Sn_5 grain by the spiral dislocation growth mechanism needs lower crystal growth energy than the two-dimensional nucleation and growth mechanism. Therefore, the mechanisms of continued growth on the rough surface and spiral dislocation growth are both play important roles in the growth of IMC grain. As a result, Cu_6Sn_5 grains have a long and thin plane top, namely plane structure, under air cooling condition as shown in Fig.3(g, k).

The degree of supercooling is the lowest under furnace cooling condition, while the solidification time is the longest among the three cooling conditions. Thus, there is sufficient time for the growth of Cu_6Sn_5 grain through all the three growth mechanisms. Namely, Cu and Sn atoms have enough time diffusing to the location of spiral dislocation and growing along c-axis in compliance with spiral dislocation growth mechanism in the vertical direction. Because the side energy of the spiral dislocation step is lower and easy to adsorb atoms to grow at the side of step by two-dimensional nucleation and growth mechanism. Therefore, the prismatic top of Cu_6Sn_5 grains could get coarsening in the horizontal direction by the mechanism of two-dimensional nucleation and growth and continue growth on the rough surface in the horizontal direction. So, all the three growth mechanisms are involved in the IMC growth under furnace cooling. Finally, the prismatic top of Cu_6Sn_5 grains grow longer and thicker under furnace cooling condition as shown in Fig.3(d, h, l).

On the basis of the above analysis, it is certified that the secondary growth of Cu_6Sn_5 has a significant effect on the morphology transformation of Cu_6Sn_5 grains at the cooling stage of soldering. In addition, the above three growth mechanisms are affected by the degree of supercooling at the soldering interface. Since the cooling rates used in the previous interfacial IMC growth models did not consider a unified regulation, the difference of the cooling rate might have influenced the accuracy of the growth model. Comparing with the previous interfacial IMC growth models, the new growth mechanisms proposed are more accurate and credible because of considering all the factors. Therefore, it is realistic to control the growth of IMC by controlling the cooling rate. For this condition, we can take advantage of the new IMC growth mechanism to obtain the appropriate morphology and thickness of IMC, which is able to improve the microelectronic soldering reliability.

4. Conclusions

In this study, the effect of the degree of supercooling on the growth mechanism of Cu_6Sn_5 grain in Sn/Cu solder joint was studied. The conclusions were summarized as follows:

1. The morphologies of Cu_6Sn_5 grains are scallop-like under high-pressure air and water cooling, while scallop-like with a plane structure and prismatic top are for air cooling and furnace cooling. In addition, synchrotron radiation in-situ imaging technology provides a strong evidence that the growth of Cu_6Sn_5 grain includes two stages: primary growth at the heat preservation stage and secondary growth at the cooling stage, and the secondary growth determines the final morphologies of Cu_6Sn_5 grains.

2. The nucleation of secondary growth on the surface of Cu_6Sn_5 grain is affected by the degree of supercooling (ΔT). When ΔT is sufficiently big, the homogeneous nucleation can easily occur, namely, two-dimensional nucleation and growth. But for a small amount of ΔT , the heterogeneous nucleation is easier than homogeneous nucleation, such as the continuous growth on the rough surface and spiral

dislocation growth.

3. The three growth mechanisms are proposed to explain the different IMC morphologies formed at soldering interface, namely, continuous growth mechanism on the rough surface(M1), spiral dislocation growth(M2), and two-dimensional nucleation and growth mechanism(M3). That is to say, the scallop-like grains are mainly controlled by the mechanism of (M1); the scallop-like with a plane structure top grains are a combined effect of the mechanisms of (M1) and (M2); the scallop-like with a prismatic top grains are controlled by all the three growth mechanisms(M1,M2,M3).

4. The three growth mechanisms are all affected by the degree of supercooling (ΔT) at soldering interface. That is, the continuous growth on the rough surface is the main growth mechanism under water cooling; the continuous growth on the rough surface and spiral dislocation growth are playing a positive role under air cooling; all the three growth mechanisms are involved under furnace cooling.

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Figure Captions

Fig.1 Schematic diagrams of (a) reflow soldering sample, (b) liquid solder removed by high-pressure air and (c) configuration for synchrotron radiation experiment

Fig.2 The furnace cooling curve during the cooling stage of soldering

Fig.3 SEM images of top -view of Cu_6Sn_5 and the soldering time is 1min. (a. 523K (250°C) high-pressure air, b. 523K (250°C) water cooling, c. 523K (250°C) air cooling, d. 523K (250°C) furnace cooling, e. 548K (275°C) high-pressure air, f. 548K (275°C) water cooling, g. 548K (275°C) air cooling, h. 548K (275°C) furnace cooling, i. 573K (300°C) high-pressure air, j. 573K (300°C) water cooling, k. 573K (300°C) air cooling, l. 573K (300°C) furnace cooling

Fig.4 SEM images of cross-section of Cu_6Sn_5 and the soldering time is 1min. (a. 523K (250°C) high-

570 pressure air, b. 523K (250°C) water cooling, c. 523K (250°C) air cooling, d. 523K (250°C) furnace
 571 cooling, e. 548K (275°C) high-pressure air, f. 548K (275°C) water cooling, g. 548K (275°C) air cooling,
 572 h. 548K (275°C) furnace cooling, i. 573K (300°C) high-pressure air, j. 573K (300°C) water cooling, k.
 573 573K (300°C) air cooling, l. 573K (300°C) furnace cooling
 574 Fig.5 The synchrotron radiation images of Sn/Cu joints at 523K, 548K, and 573K (250°C, 275°C and
 575 300°C) with 60min. (a₁~c₁) and (a₂~c₂) are the end of heat preservation and furnace cooling during
 576 soldering.
 577 Fig.6 Schematic diagrams of (a-f) growth process of spiral dislocation around spiral dislocation source
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