EFFECT OF Al ADDITION TO IMC FORMATION, MECHANICAL AND WETTING PROPERTIES OF LOW-Ag SAC SOLDER ALLOY

by

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TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ag	Argentum (silver)
Al	Aluminium
Al_2O_3	Aluminium Oxide
ASTM	American Society for Testing and Materials
Bi	Bismuth
BSE	Backscattered Electron
CH_4O	Methanol
CTE	Coefficient Thermal Expansion
cm	Centimeter
Cu	Copper
DSC	Differential Scanning Calorimetry
EDX	Electron Dispersive X-Ray Spectroscopy
Fe	Ferum (iron)
Fe-SEM	Field Emission Scanning Electron Microscope
$FeCl_3$	Ferric Chloride
FR-4	Flame Retardant-4
g	gram (weight)
Ga	Gallium
Ge	Germanium
HCl	Hydrochloric acid
HNO_3	Nitric acid
H_2O	Water

IMC	Intermetallic Compound
In	Indium
JEDEC	Joint Electron Device Engineering Council
JEITA	Japan Electronics and Information Technologies Industries Association
JIS	Japanese Industrial Standard
kN	kilo Newton
mg	milligram
min	minute (time)
mm	millimeter (length)
µm	micrometer
Mo	Molybdenum
MPa	Mega Pascal (stress)
Ni	Nickel
N_2	Nitrogen
Pd	Palladium
Pb	Plumbum (lead)
Pt	Platinum
PTH	Pin Through Hole
PCB	Printed Circuit Board
PWB	Printed Wiring Board
RA	Rosin Activated
ROHS	Restriction of Hazardous Substances
s	second (time)

SAC	Sn-Ag-Cu
SAC0305	Sn-0.3Ag-0.5Cu
SAC105	Sn-1Ag-0.5Cu
SAC205	Sn-2Ag-0.5Cu
SAC107	Sn-1Ag-0.7Cu
SAC0507	Sn-0.5Ag-0.7Cu
SAC157	Sn-1.5Ag-0.7Cu
SAC127	Sn-1.2Ag-0.7Cu
SAC305	Sn-3Ag-0.5Cu
SAL	Sebatian Antara Logam
Sb	Antimony
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SiC	Silicon Carbide
SMT	Surface Mount Technology
Sn	Stanum (tin)
SnO	Tin Oxide
SnPb	Lead-tin
SiC	Silicon Carbide
Ti	Titanium
WEEE	Waste Electronic and Electrical Equipment
XRF	X-Ray Fluorescent
Zn	Zinc

LIST OF SYMBOLS

A	Area
at.%	Atomic percent
β-Sn	Sn-rich phase
d	IMC thickness after aging
d_o	Initial IMC thickness
D	Diffusion coefficient
D_o	Intrinsic diffusivity
F	Shear load
F	Wetting force
F_b	Buoyancy force
F_e	End force
F_{max}	Maximum wetting force
F_w	Withdrawal force
g	Gravitational acceleration
J	Joule
m	meter
µ	Micron
N	Newton
P	Perimeter of substrate
Q	Activation energy
R	Gas constant

S_b	Ratio of wetting force just before withdrawal to the wetting force during complete wetting
t	Aging time
t_1	Wetting time
T	Temperature
T_c	Crystallization temperature
T_m	Melting temperature
T_{oc}	Onset crystallization temperature
T_{om}	Onset melting temperature
τ	Shear strength
V	Volume
wt.%	Weight percent
θ	Wetting angle
γ	Surface tension of solder
γsg	Surface tension between solid and gas
γsl	Surface tension between solid and liquid
γlg	Surface tension between liquid and gas
ρ	Density
$^{\circ}C$	Degree celcius
%	Percentage

KESAN PENAMBAHAN Al KEPADA PEMBENTUKAN SEBATIAN ANTARA LOGAM (SAL), SIFAT-SIFAT MEKANIKAL DAN PEMBASAHAN ALOI PATERI RENDAH Ag

ABSTRAK

Kesan penambahan Al dalam peratusan yang berbeza terhadap mikrostuktur, pembentukan sebatian antara logam (SAL), sifat-sifat mekanikal dan pembasahan aloi pateri Sn-0.3Ag-0.5Cu (SAC0305) telah dikaji. SAC0305, SAC-0.5Al, SAC-1Al, SAC-1.5Al dan SAC-2Al telah disediakan dengan kaedah tuangan. Aloi pateri telah dipateri di atas substrat Cu pada suhu 260 ^{o}C selama 10 saat. Komposisi setiap aloi pateri telah ditentukan menggunakan teknik pendarfluor sinar-X (XRF). Kalorimeter imbasan perbezaan (DSC) telah digunakan untuk menilai sifat-sifat terma manakala ujian kebolehbasahan dan sebaran telah dijalankan untuk menganalisis kebolehbasahan. Mikrostruktur pateri pukal dan lapisan SAL telah diperhati menggunakan mikroskop elektron imbasan (SEM) yang dilengkapi dengan EDX. Sementara itu, ujian ricih bola telah dijalankan untuk menilai kebolehharapan sambungan pateri itu. Kebolehbasahan berkurang dengan penambahan Al, tetapi masih di dalam julat yang boleh diterima. Penambahan Al menyebabkan pembentukan SAL Ag_3Al dan Cu-Al, pengurangan kuantiti SAL Ag_3Sn dan Cu_6Sn_5, dan pengecilan saiz dendrit β-Sn. Penambahan Al melebihi 1 wt.% menyebabkan pembentukan partikel Al primer. Kuantiti SAL Ag_3Al dan Cu-Al bertambah dengan penambahan amaun Al. Aloi pateri dengan penambahan Al memberikan lapisan SAL yang lebih nipis (0.62 µm hingga 1.15 µm) berbanding SAC0305 (2.39 µm) untuk keadaan sampel selepas pateri dan juga selepas penuaan isoterma. Kekuatan ricih bagi aloi pateri yang telah ditambah dengan Al yang berada di

dalam julat 19.96 MPa hingga 21.93 MPa adalah lebih tinggi berbanding dengan SAC0305 (19.21 MPa) tetapi lebih rendah berbanding dengan SAC305 (35 MPa). SAC-1Al telah dikenalpasti sebagai aloi pateri terbaik berbanding empat jenis aloi pateri yang lain kerana SAC-1Al mempunyai mikrostruktur yang halus, lapisan SAL yang nipis, kebolehbasahan dalam julat yang boleh diterima dan kekuatan ricih yang tinggi.

EFFECT OF Al ADDITION TO IMC FORMATION, MECHANICAL AND WETTING PROPERTIES OF LOW-Ag SAC SOLDER ALLOY

ABSTRACT

The effect of various percentages of Al addition to the microstructure of bulk, intermetallic compound (IMC) formation, wetting properties and mechanical properties of Sn-0.3Ag-0.5Cu (SAC0305) solder alloy was investigated. SAC0305, SAC-0.5Al, SAC-1Al, SAC-1.5Al and SAC-2Al were prepared via casting process. The solder alloys were reflowed onto Cu substrate at 260 °C for 10 seconds. The composition of each solder alloys were determined using XRF. DSC was used to evaluate the thermal characteristics while wetting balance test and spreading test were used to analyze the wettability. The microstructures of the bulk solder as well as the interfacial IMC layer were observed using SEM equipped with EDX. Meanwhile, ball shear test was carried out to assess the reliability of the solder joints. The wettability of solder alloys decreased with the increasing amount of Al, but still within the acceptable range. Addition of Al resulted in the formation of Ag_3Al and Cu-Al IMC, lowered the amount of Ag_3Sn and Cu_6Sn_5 IMC and refined β-Sn dendrites. Further addition of Al above 1 wt.% resulted in the formation of primary Al particles. The amount of Ag_3Al and Cu-Al IMC and primary Al particles increased with increasing amount of Al. The Al-added solder alloys gave thinner IMC layer (0.62 µm to 1.15 µm) at the solder joint compared to SAC0305 (2.39 µm) for as reflowed conditions and also after isothermal aging. The shear strength of Al added solder alloys which ranging from 21.93 MPa to 19.96 MPa were higher than SAC0305 (19.21 MPa) but lower than SAC305 (35 MPa). SAC-1Al was found to be the

best solder alloy compared to the other four due to its fine microstructure, thin IMC layer, acceptable wetting and high shear strength.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The toxicity of lead has been discussed for nearly 90 years since the year 1930. Various published researches have revealed that lead is harmful not only to the environment, but also to human health (Cory-Slechta et al., 1983, Davies et al., 1976, Mahaffey, 1990, Pounds et al., 1991, Spehar et al., 1978, Todd et al., 1996). Driven by these concerns and international legislation, electronic manufacturing companies and researchers have been concentrating their efforts in fabricating lead free solder to replace the Sn-Pb solder.

There are binary, ternary and quaternary solder alloys with Sn as their based material. The most common binary solder alloys are Sn-Ag, Sn-Cu, Sn-Bi, Sn-In and Sn-Zn solder alloys. For ternary solder alloys, Sn-Ag-Cu and Sn-Ag-Bi are the most common types of solder alloy. However, each of these solder alloys holds certain disadvantages including reliability and cost issues, too high or too low melting temperature and low to moderate wetting. As for the quaternary solder alloys, Al, Ni, Ga and Sb are commonly added to improve their mechanical properties.

According to IPC Solder Value Product Council, among these solder alloys, the Sn-Ag-Cu (SAC) solder alloy is found to be the most suitable candidate to replace the traditional Sn-Pb in surface mount technology (SMT) assembly (Graedel, 2002, Higgins III, 2002, Anderson, 2007). Generally, SAC solder alloy has better shock resistance, improved functionality, higher reliability and environmentally friendly. Sn-3Ag-0.5Cu (SAC305) solder alloy is commonly use for reflow soldering. However, SAC305 solder alloy can cause negative results in wave soldering and hand soldering where it often suffer from hot tears or also known as shrink holes. This defect causes difficulties in quality inspections as it is difficult to distinguish between bad or good joint.

Moreover, the cost of SAC305 solder alloy is far higher than Sn-Pb solder and among the highest compared to other lead-free solder alloys due to its high silver content (Lee, 1997). Therefore, manufacturers shifted to the cheaper alternative which is the using of Sn-Cu solder with the minor addition of nickel and bismuth. Sn-Cu-Ni solder alloy has been patented by Nihon Superior while Sn-Cu-Ag-Bi has been patented by Alpha Metals. Both of these solder alloys have improved wetting and reliability compared to Sn-Cu solder alloy. These types of solder alloys also widely used in wave and hand soldering.

Another approach to reduce cost is by reducing the silver content to below than 2 wt.% in the SAC solder system. This type of solder is known as low-Ag content SAC solder. The common low-Ag SAC solders are SAC105, SAC205, SAC107 and SAC0507. Low-Ag SAC solder not only helps to reduce cost but also issues related to brittle fracture of the SAC305 solder due to the formation of large amount of brittle Ag_3Sn phase with higher content of Ag. This will give more ductile and compliant solder for high impact condition compared to the high-Ag content SAC solder.

1.2 Problem Statement

Although low Ag content gives advantages in term of reducing Ag_3Sn intermetallic compound (IMC) and cost reduction, it also has some drawbacks. The reduction of Ag content gives rise to more primary β-Sn phase (large β-Sn grains). β-Sn grains are soft and ductile compared to the IMC. Hence, the solder strength of low Ag content SAC alloy is lower than that of high Ag-content SAC solder alloys. In order to solve the issue, several studied have been conducted by adding alloying elements such as In, Ni, Bi, Sb and Pd.

Kanlayasiri et al. (2009) have added 0.5 to 3.0 wt.% In into Sn-0.3Ag-0.5Cu (SAC0305) solder alloy and they discovered that Sn-rich phase became finer with more uniform distribution of IMC. The same result has been obtained by adding 0.05 wt.% Ni into Sn-1.5Ag-0.5Cu solder (Hammad, 2013). Yong-Sung et al. (2007) have added 0.5 wt.% Sb into Sn-1.2Ag-0.5Cu and they have found that it gave high ductility and high drop test reliability compared to Sn-1.2Ag-0.5Cu and SAC305 solder alloys. El-Daly et al. (2015) have reported that adding 1 wt.% Bi into Sn-1.5Ag-0.7Cu (SAC157) have refined the microstructure thus increased the elastic modulus, ultimate tensile strength and yield strength of the solder alloy. The addition of 0.03 wt.% Pd together with 0.4 wt.% In into Sn-1.2Ag-0.7Cu (SAC127) have also been reported give the same results (Yu et al., 2010). However, In, Pd, Bi, Ni and Sb are among the high cost elements due to their limited availability.

On the other hand, Al is a cheap material due to its abundant availability as well as environmentally friendly. Its low melting temperature also is expected to give small difference to the melting temperature of the conventional SAC305 solder alloy thus lead to minor or even zero alteration to the reflow profile during vast manufacturing process Furthermore, several studies have reported that it can refines the microstructure and suppress the growth of the interfacial IMC layer thus improve the reliability and wettability of the solder (Young-Kun et al., 2008, Sabri et al., 2013, Sabri et al., 2014)

There were limited reported studies about the addition of Al into the low-Ag SAC (< 2 wt.% Ag) solder. Sabri et.al (2013) has added 1.0 to 2.0 wt.% Al into Sn-1Ag-0.5Cu (SAC105) and they found that the Al suppressed the formation of Ag_3Sn an Cu_6Sn_5 IMC phases. However, the total elongation of the solder significantly decreased and it shifted from ductile failure to the undesirable brittle failure via intergranular cracking mechanism. Furthermore, another study reported by Sabri et. al (2014) has found that the addition of 0.5 wt.% Al into the SAC105 did not enhance the aging resistance of the solder alloy, resulted in notable degradation of the mechanical properties.

Therefore, this project focuses on various percentages of Al addition to the extreme low-Ag content SAC (0.3 wt.% Ag) solder system to investigate their effect on microstructure of the bulk solder and IMC formation at the solder joint that eventually will affect the wettability and mechanical properties (shear strength) of the solder alloy.

1.3 Objectives

The primary objectives of the project are as follows:

i. To study the effect of Al addition on the microstructure of bulk low-Ag SAC solder alloys.

ii. To evaluate the IMC formation at the solder-substrate interface of low-Ag SAC and its Al added solder alloys before and after isothermal aging

iii. To evaluate the wetting and mechanical properties of Al added low-Ag SAC solder alloys.

1.4 Scope of Research

The project was done by adding 0.5, 1.0, 1.5 and 2.0 wt.% Al into the Sn-0.3Ag-0.5Cu (SAC0305) to evaluate the effect of Al to the microstructure of bulk solder as well as the IMC layer formation at the solder-copper substrate interface before and after isothermal aging. Comparisons in terms of thickness, morphology and distribution of the IMC at the solder joint and within the bulk solder were done between all five types of solder alloys. The microstructure of the bulk solder and the solder joint was characterized using Fe-SEM and EDX.

Thermal properties of the solder alloys were analyzed using DSC. Spreading test and wetting balance test were used to check the wettability of the solder alloys in terms of spreading area, wetting angle, wetting time and wetting force. Reliability of the solder alloys was evaluated using ball shear test with different shear rate. The fracture surface was observed using Fe-SEM and EDX in order to analyze the failure mode of the specimens.

In this project, the conventional SAC305 has been set as the reference material. All of the results obtained were compared with SAC305 to evaluate the properties of the fabricated solder alloys. Finally, comparison between all five types of solder alloys was done based on all the results obtained and the best amount of Al to be added into low-Ag SAC solder was chose.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Solder is a fusible metal alloy used to join metallic surfaces. Soldering is a process of joining two or more metals by heating the solder alloy above its melting temperature and flow the molten solder into the joint. There are many different types of solder alloys. $Ga_{62.5}In_{21.5}Sn_{16}$ solder alloy has been reported to have the lowest liquidus temperature which is 10.7 °C while $Ge_{55}Al_{45}$ solder alloy has the highest liquidus temperature which is 424 °C (Vianco and Rejent, 1999). Generally, solder materials can be categorized into three different groups as shown in Table 2.1.

Table 2.1: Classification of solders based on their melting temperature

Solder	**Melting temperature (°C)**
Low temperature solder	≤ 138
Mid-range temperature solder	$138 < t \leq 235$
High temperature solder	$235 < t \leq 450$

2.1.1 Sn-Pb Solder

The eutectic 63Sn-37Pb and the nearly eutectic 60Sn-40Pb solder alloys have been widely used since the early 20th century due to their outstanding properties. Sn-Pb solder alloy is classified under mid-range temperature solder with an ideal melting temperature of about 183 °C, possessing excellent electrical, mechanical, chemical and thermal properties (Glazer, 1994, Islam et al., 2005, Thomas Siewert et al., 2002). Sn-Pb solder is widely used in plated through hole (PTH) and surface mount technology

(SMT) for mass productions. Application wise, due to its low melting temperature, it is mostly used in computer and telecommunication devices where minimum heat may be applied. However, due to its low creep resistance, the 63Sn-37Pb is often being modified by the addition of 1.4 wt.% Ag.

2.1.2 Lead-free Motivation

Transition from lead-tin solder to lead-free solder is mainly due to health and environmental concern. The toxicity of lead as a heavy metal has been discussed since the year 1930 (Davies et al., 1976, Spehar et al., 1978, Cory-Slechta et al., 1983, Mahaffey, 1990, Pounds et al., 1991, Todd et al., 1996). Leakage of leaded toxicity may occur during disposition of lead-contained devices that may contaminate the water source and subsequently, consumed by other living things including human. Latest study revealed that lead can affect human's nervous system especially during fetal period and infancy (Finkelstein et al., 2014).

Because of these concerns, in 1991 the U.S. Congress and U.S Senates have taken an initiative to limit the lead-based products by increasing the tax for lead containing product. Later in February 2003, the European Union put the legislation into force via directives on Waste Electrical and Electronic Equipment (WEEE) and Restriction on the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS). These directives stated that all electrical and electronic appliances must be lead-free starting from July 1st 2006 (COUNCIL, 2003a), except for military products and implanted medical devices (COUNCIL, 2003b).

Different legislation with the same objective has also been developed in Japan and United States. In the year 2000, Japan Electronics and Information Technologies Industries Association (JEITA) has developed a guideline for Japanese Industry with three major recommendations (JOM, 2002):

(1) 1999: Introduction of lead-free solder in products

(2) 2002: General use of lead-free solder in products

(3) 2005: Lead-free solder in all products, with some exceptions.

Another factor that leads to the conversion for lead-free solder is the international marketing pressure. Companies with lead-free products would market their products as environmentally friendly and consumers usually prefer them over lead contained products (aimsolder, 2005). The above mentioned legislations and marketing pressure forced electronic manufacturing companies and researchers to find alternative materials to the lead-tin solder.

2.1.3 Soldering Technology

Soldering became the most common method for electrical connections after the existence of printed circuit board (PCB), wiring board and assembly process in the early 1907. Various soldering processes have been developed mainly to improve the reliability of solder joints. Basically, mass production PCBs are mostly wave or reflow soldered, though hand soldering process is still a standard practice for many other applications.

2.1.3.1 Wave Soldering

Wave soldering is a soldering technique that can be used for both through-hole printed circuit assemblies as well as surface mount. PCB is placed on top of a conveyor that moves the PCB through 4 different zones (Tarr, 2008):

(1) Fluxing zone. Flux is sprayed to the PCB in order to clean the surface and remove oxide layers prior to soldering

(2) Preheating zone. Hot air is blown to the PCB to activate the flux and to prevent thermal shock.

(3) Soldering zone. A quantity of molten solder inside a tank contacts the bottom of the board and stick to the solder pads. Nitrogen (N_2) gas was used to reduce oxidation from the surface of solder. This will help to improve the quality of joint formed.

(4) Cooling zone. The PCB is cooled to room temperature at a reasonable rate. The PCB tends to warp if the cooling process is too quick whereas it will become brittle when the cooling process is too slow.

However, precise control of the wave height is an important requirement and it has become an issue with wave soldering. Other than that, cracks and wrong solder thickness are the regular reported defects with wave soldering. Figure 2.1 shows the steps involved in wave soldering process.

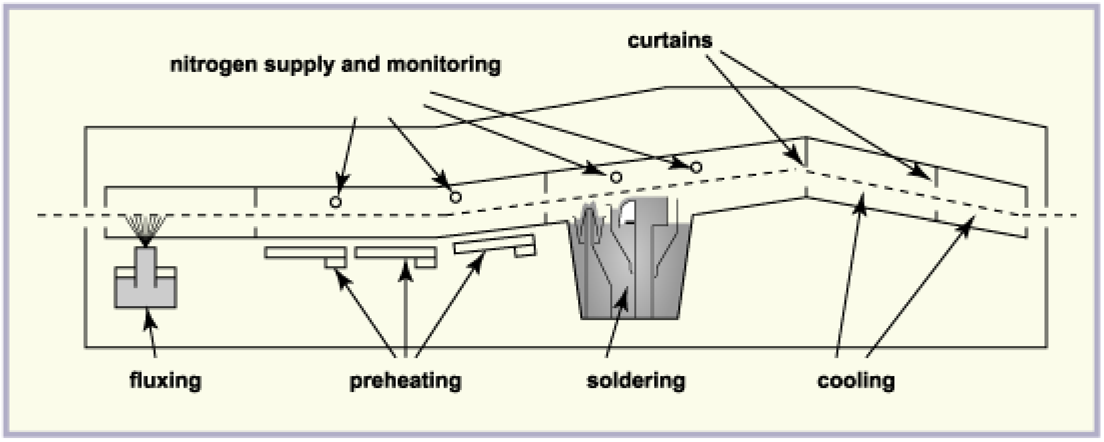

Figure 2.1: Steps involved in wave soldering process (Tarr, 2008)

2.1.3.2 Reflow Soldering

Reflow soldering is the most common soldering technique of attaching surface mount components to a circuit board. Solder paste containing solder, flux and solvent is applied to the surface of the PCB before placing the surface mount components. The solder paste acts as temporary glue that holds the components in place prior to reflow. The PCB is then heated above the melting point of the solder paste. At this point, the flux removes the oxide layer and solder joint is subsequently formed. Generally, there are three types of reflow soldering which are infrared, convection and infrared convection reflow soldering. Figure 2.2 shows the reflow soldering process.

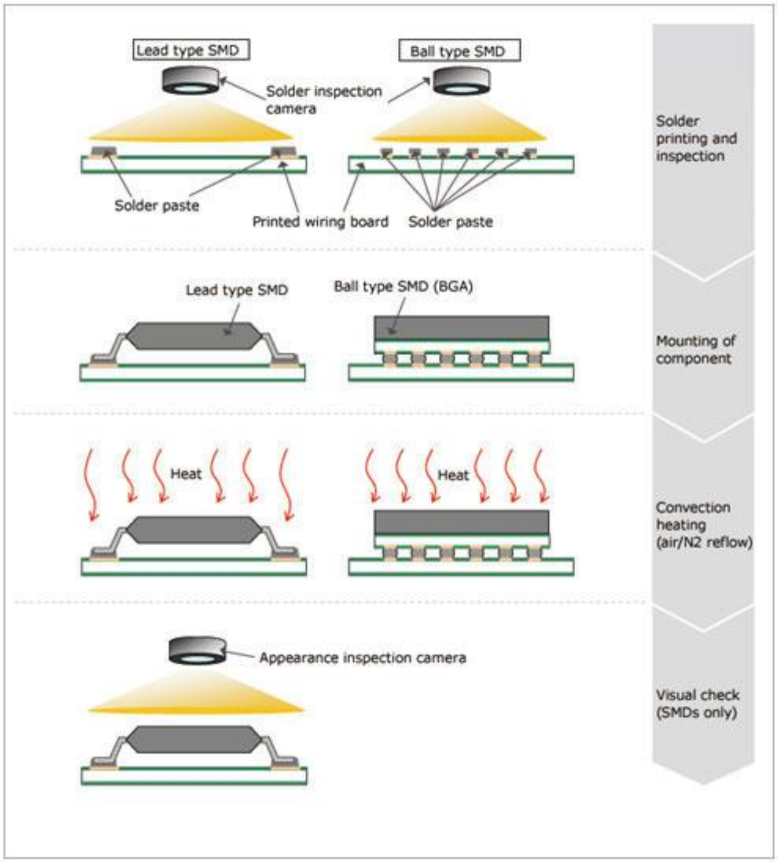

Figure 2.2: Schematic of the reflow soldering process (engineersgarage, 2011)

2.1.4 Integrated Circuit (IC) Assembly

Solder material functions as interconnect materials for component. Solder interconnect is very important in three major aspects;

(1) Electrical - Solder become a connection path from the silicon die to the substrate within the package known as 1^{st} level packaging and between different packages to copper trace on the printed wiring board (PWB) known as 2^{nd} level packaging (Shangguan, 2005).

(2) Mechanical - Solder gives mechanical support for many interconnected materials and components in terms of reliability.

(3) Thermal - Solder dissipates heat generated by the device during service together with other thermal management tools (Abtew and Selvaduray, 2000).

In 1st level packaging, wire bonded method and flip chip method are the most common methods to connect silicon die to the substrate. In wire bonded method, connections between chips are made through the board or chip carrier and back to other chips in the stack. However, this approach is limited by the size of the wire bonders. Different from wire bonded method, solder bumps are directly placed on the die surface in flip chip method. The die is then flipped so that it will have direct contact with the substrate. Flip chip method has been reported to have huge advantages over other methods such as lowest inductance, highest frequency, shortest leads and smallest device footprints (Ng, 2005, DING, 2006). The schematic images of the wire bonding method and flip chip method are shown in Figure 2.3 and Figure 2.4 respectively.

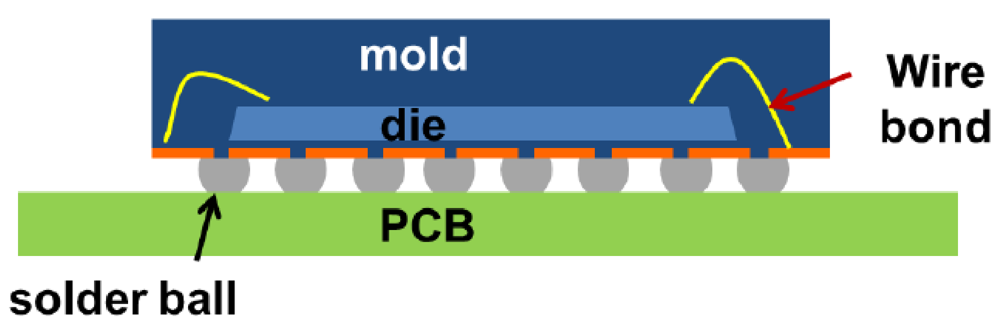

Figure 2.3: Schematic of wire bonding method (Xu, 2013)

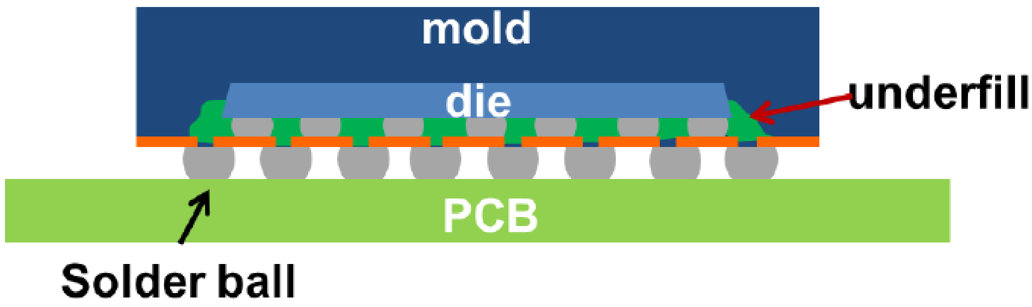

Figure 2.4: Schematic of flip chip method (Xu, 2013)

As for 2nd level packaging, the most common solder interconnect technologies are pin through hole and surface mount technology. In pin through hole method, multiple components with lead wires are led to the board through holes. The leads are then soldered to form joint. Surface mount technology is the improved technology of the pin through hole method. The components can be mounted directly on the PCB, without requiring holes. The cross section images of the pin through hole method and surface mount method are shown in Figure 2.5 and Figure 2.6 respectively.

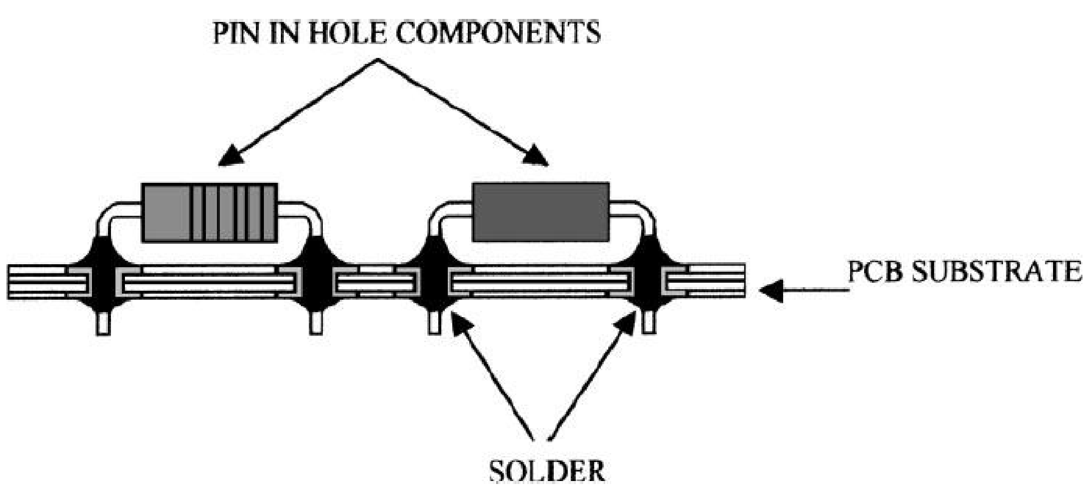

Figure 2.5: Cross section image of pin through hole method (Abtew and Selvaduray, 2000)

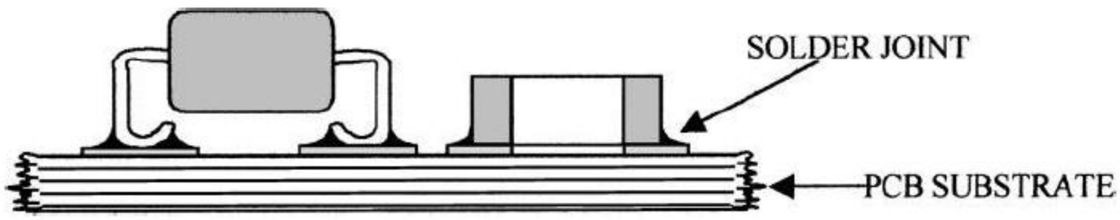

Figure 2.6: Cross section image of surface mount method (Abtew and Selvaduray, 2000)

2.2 Lead-free Solders

There are wide varieties of lead free solders that can replace the conventional Sn-Pb solder. However, the most widely used lead free solders are comprise of different amount of tin, silver and copper as their constituent elements (Anderson, 2007, Graedel and T.E., 2002, Higgins, 2002, Miyazaki, 2001). The common type of lead-free solders together with their characteristics and applications are summarized in Table 2.2

Table 2.2: Common lead-free solder alloys

Types	Solder	Characteristics	Applications
Binary alloys	Sn-Ag	- Melting temperature between 221 °C to 226 °C - Consists of globular β-Sn dendrites and large Ag_3Sn platelets - Have reliability issue - Poor wettability	- Electronic assemblies - Die attachments - Thick films (azom, 2004)
	Sn-Cu	- Cheap - Moderate wetting but sufficient for most applications	- Wave soldering (Biocca, 2006) - Printed board assemblies (Sweatman and Nishimura, 2006)
	Sn-Bi	- Low melting point - High creep resistance - Eutectic composition is brittle - Expensive	- Low temperature soldering - Step soldering (Mei and Morris, 1992)
	Sn-In	- Low melting temperature - Extreme softness and ductility - Excellent wetting properties - Poor fatigue behavior - Expensive	- Low temperature soldering - Fusible alloys - Die attachments (Chiou et al., 2013)
	Sn-Zn	- Low melting temperature - Excellent mechanical properties - Cheap - Poor wetting due to oxidation	- Reflow soldering - Aluminum assemblies - PWB (Suganuma and Kim, 2007)
Ternary alloys	Sn-Ag-Bi	- High solderability - High tensile and shear strength - High fatigue resistance - Brittle	- SMT (Yamaguchi et al., 2004)
	Sn-Ag-Zn	- Cheap - High melting temperature - High shear strength - Poor wetting	- High temperature soldering in SMT (Lee, 1997)
	Sn-Ag-Cu	- High solderability - High yield strength - Good temperature cycling reliability - Superior mechanical properties - High melting temperature - Poor wettability - Expensive	- Reflow soldering - High temperature soldering - 1st and 2nd level packaging - Electronic assemblies (Mallik et al., 2009)

2.2.1 Binary Alloys

Binary lead free alloys are usually preferable since most of them have eutectic composition that is characterized by equivalent solidus and liquidus temperature. It also has single melting temperature, hence minimizing the possibility for compositional segregation and hot tearing that can deteriorate the mechanical properties. In addition, they have simple microstructure with at most two different phases, hence, reducing the likelihood of the phases form uncontrollably during solidification. Sn-Ag, Sn-Cu, Sn-Bi, Sn-In and Sn-Zn are among the solder alloys that have attracted researcher's attention due to their various advantages.

2.2.1.1 Sn-Ag Solder

The Sn-Ag solder system with the Sn content of more than 90% and Ag content between 1 to 4% is among the most widely used lead free solders in industries. Its melting temperature ranging between 221 $^{\circ}$C to 226 $^{\circ}$C, depending on the amount of Ag. Figure 2.7 shows the phase diagram of Sn-Ag system. It could be seen in the phase diagram that the eutectic composition is Sn-3.5%Ag with the eutectic temperature of 221 $^{\circ}$C. The solidified Sn-Ag solder consists of globular β-Sn dendrites with large Ag_3Sn IMC platelets occupying the interdendritic region (McCormack and Jin, 1994). These large, brittle Ag_3Sn IMC platelets lead to reliability issue for the Sn-Ag binary system as Ag_3Sn act as stress concentrator that can initiate crack (Kim et al., 2003). Other than that, due to its relatively high melting temperature and manufacturing cost, as well as poor wettability, minor alloying elements were commonly added to the Sn-Ag system such as Cu, Zn and Bi. These alloying elements have reduced the melting temperature and improved the reliability and wettability of Sn-Ag system (Islam et al., 2005).

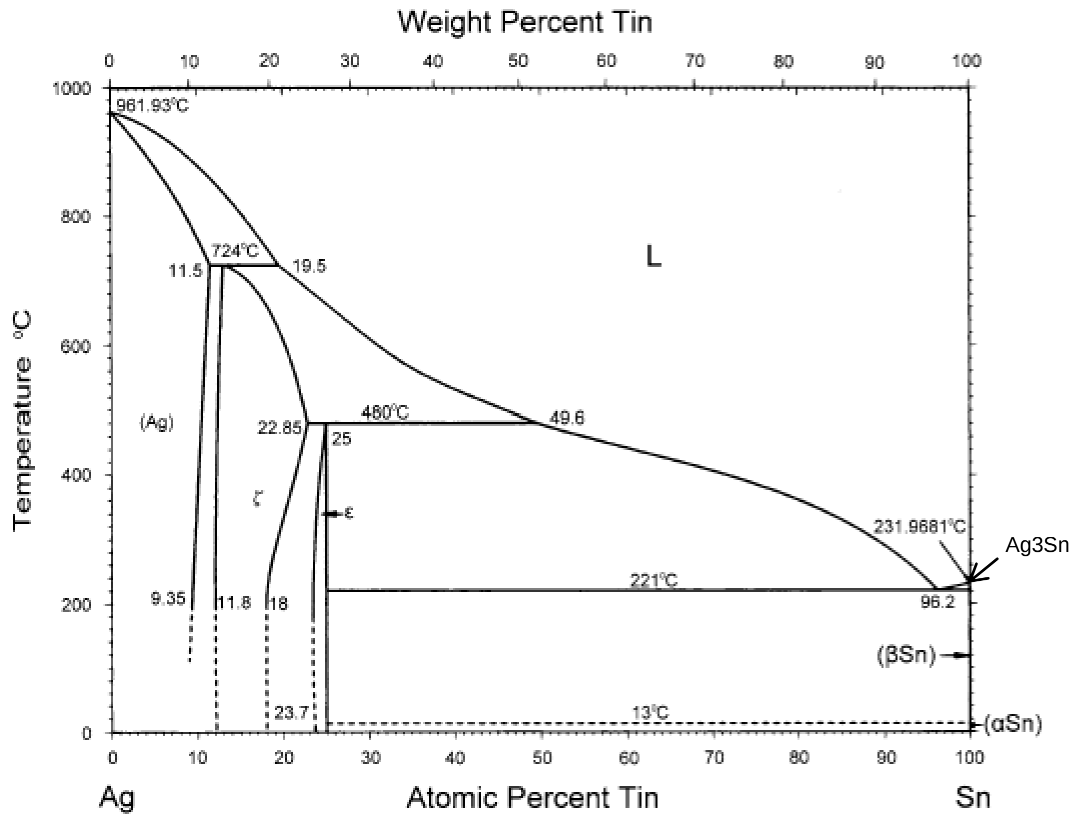

Figure 2.7: Sn-Ag binary phase diagram (Chen et al., 2007)

2.2.1.2 Sn-Cu Solder

Figure 2.8 shows the Sn-Cu binary phase diagram. The phase diagram showed that the eutectic temperature of the system is approximately 227 °C and the amount of Cu is 0.7 %. Sn-Cu binary solder is reasonably cheaper than Sn-Ag binary solder due to abundant availability of Sn and Cu. It is now among the low cost solder that is attracting attention worldwide. Moreover, it posses moderate wetting but considered sufficient for most applications (Satyanarayan and Prabhu, 2011).

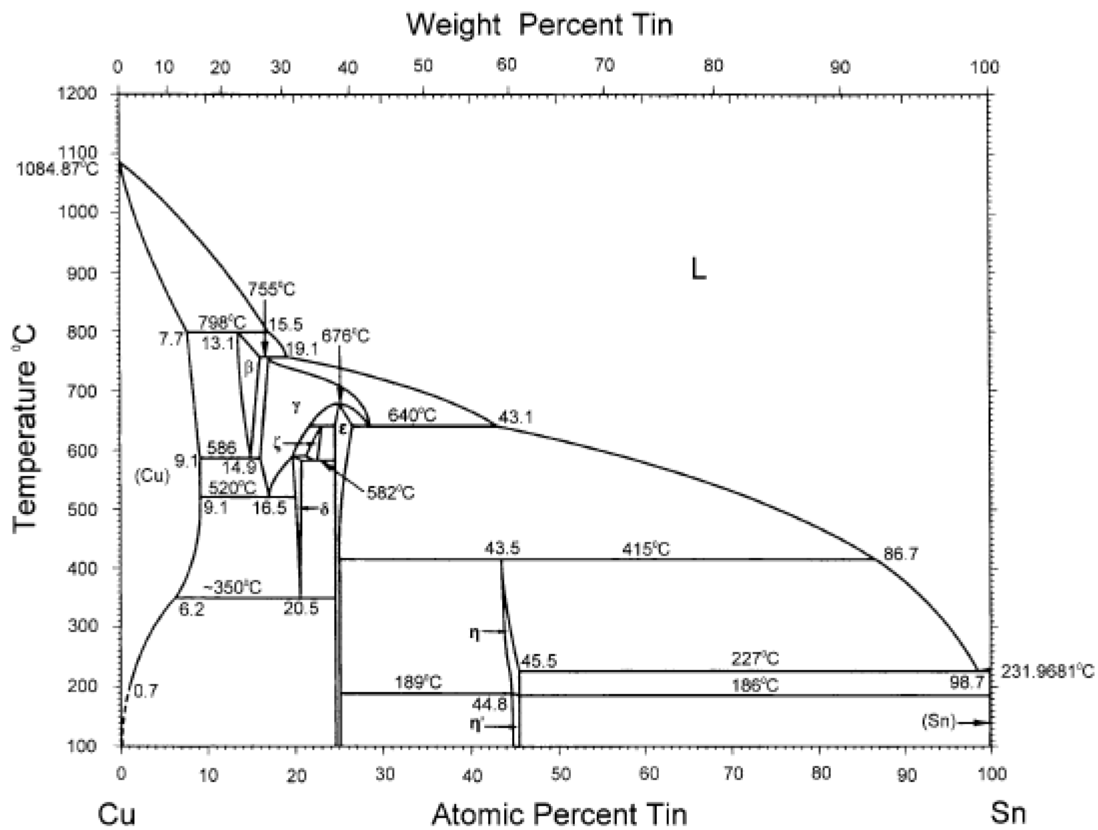

Figure 2.8: Sn-Cu binary phase diagram (Chen et al., 2007).

2.2.1.3 Sn-Bi Solder

According to the Sn-Bi phase diagram shown in Figure 2.9, the eutectic composition is Sn-57% Bi with eutectic temperature of approximately 139 °C. Due to its low melting point, Sn-Bi solder is favored for low soldering temperature applications (Bath, 2007). The eutectic composition of Sn-Bi solder was reported to be brittle particularly under impact loading and rapid stressing due to the brittle nature of Bi (Bath, 2007, Osório et al., 2013). Therefore, in between the year 1990 and 2000, electronic industries have chosen Sn-3 wt.% Bi solder alloy via trial and error in order to minimize the brittleness of the solder (Wu et al., 2000, Shiue et al., 2003). Other than that, due to the lack of availability of Bi, the Sn-Bi binary solder cost higher than other binary solder system.

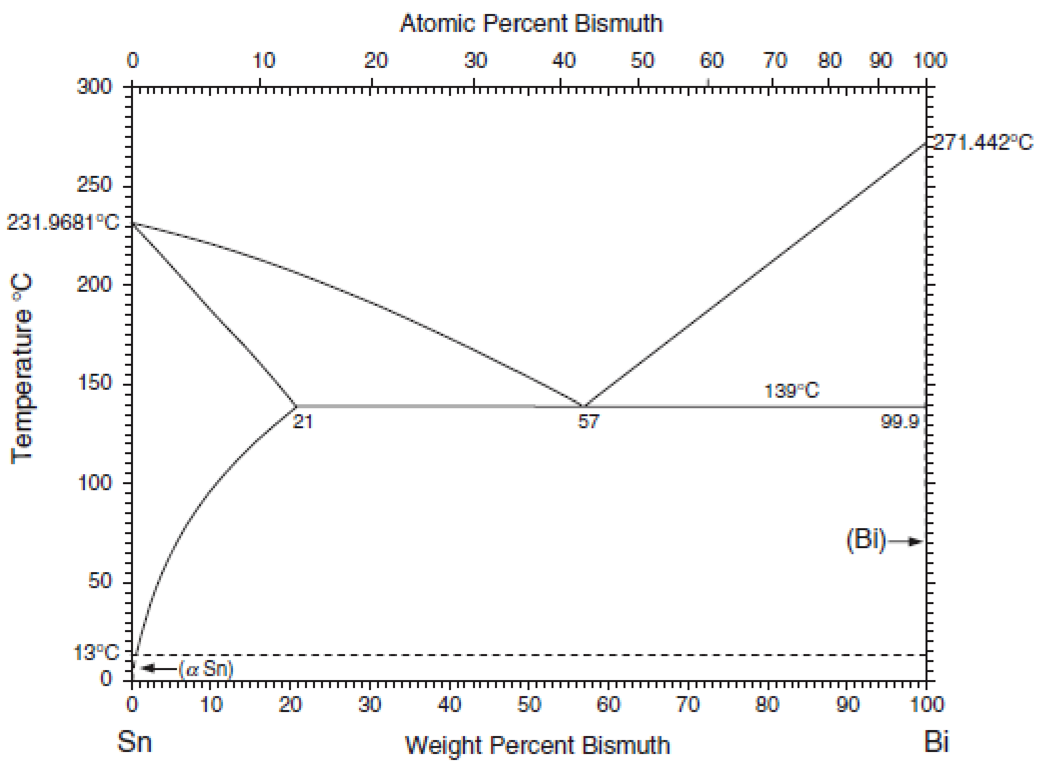

Figure 2.9: Sn-Bi binary phase diagram (Chen et al., 2007).

2.2.1.4 Sn-In Solder

In-48Sn is the eutectic composition of Sn-In solder with a melting temperature of 118 °C. Due to its considerably low melting temperature, extreme softness and ductility and excellent wetting properties, Sn-In solder is suitable for low temperature solders and fusible alloys. However, it has tendency to cold weld and displays poor high temperature fatigue behavior (Zoran Miric and Grusd, 1998) due to its extreme softness.

Furthermore, it is not economically feasible to replace Sn-Pb solder as the limited availability of In resulted in higher manufacturing cost (Kang, 2004).

2.2.1.5 Sn-Zn Solder

Sn-Zn phase diagram in Figure 2.1 showed that the eutectic composition for Sn-Zn system is Sn-8.8Zn with its melting temperature of 198.5 °C (Chen et al., 2007). Sn-9Zn binary solder melts at 198 °C which is considerably low melting temperature, possess excellent mechanical properties as well as low cost. However, Yangshan et al. (2005) have reported that the major problem with Sn-Zn solder is wetting and oxidation. Zn causes oxidation and corrosion and it reacts with flux to form a hardened paste, resulting in fairly reactive Sn-9Zn solder (Islam et al., 2005). Typically, Sn-9Zn solder is used for soldering aluminum assemblies. However, it cannot be used for microelectronic applications because they readily oxidized during soldering which cause poor wetting (Kang, 2004).

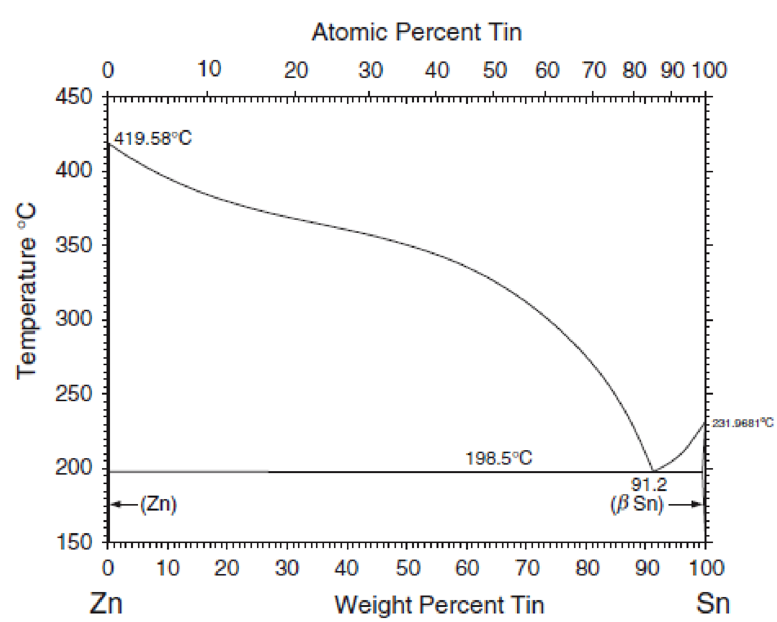

Figure 2.10: Sn-Zn binary phase diagram (Chen et al., 2007)

2.2.2 Ternary Alloys

Although binary lead free solders are more preferable, there were limited numbers of the binary eutectic composition solder available. Furthermore, the additions of another alloying element to the binary solder system can give more variations to improve the mechanical properties of the solder alloys such as via solid solution and precipitation hardening. Sn rich phase in the eutectic Sn-Ag binary solder system was considered the most potential for alloy modification via ternary addition (Vianco and Rejent, 1999). Bi and Zn are the common added alloying element into the Sn-Ag binary solder system.

2.2.2.1 Sn-Ag-Bi Solder

Sn-Ag-Bi solder with Bi composition ranging from 1% to 5% melts between 208 °C and 215 °C due to low melting point of Bi which is 271 °C. Furthermore, less than 5% Bi content exhibited higher solderability compared to other lead free solder alloys (Vianco and Rejent, 1999, Moser et al., 2001, Takao and Hasegawa, 2001, Choi et al., 2002, Hwang and Suganuma, 2004). It has also been reported that the addition of 1% to 6% Bi increased the tensile and shear strength of the solder as well as its fatigue resistance (Kariya and Otsuka, 1998b, Kariya and Otsuka, 1998a, Choi et al., 2002, Hwang and Suganuma, 2004, Shang et al., 2007, Subramanian, 2012). However, the addition of Bi also resulted in more brittle solder (Shang et al., 2007, Subramanian, 2012). On top of that, Sn-Ag-Bi solder cannot sustain heat generated from actual operation as Bi is easily oxidized (Shiue et al., 2003). Figure 2.11 and Figure 2.12 shows the Sn-Ag-Bi ternary phase diagram and the liquidus projection of the system respectively. The eutectic ternary of Sn-Ag-Bi system is at point A with the melting temperature increase with the increasing amount of Ag. Figure 2.12 also showed that Ag_3Sn IMC is the possible IMC that will form when the amount of Ag increase.

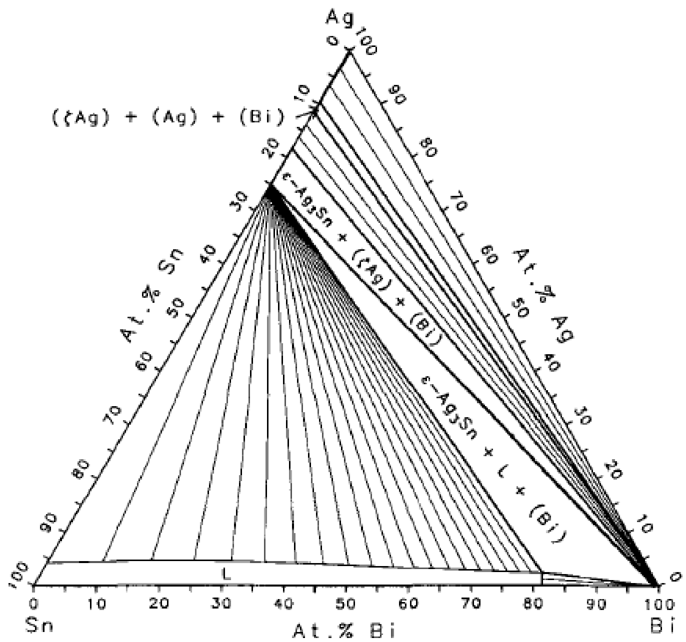

Figure 2.11: Sn-Ag-Bi ternary phase diagram (Kattner and Boettinger, 1994)

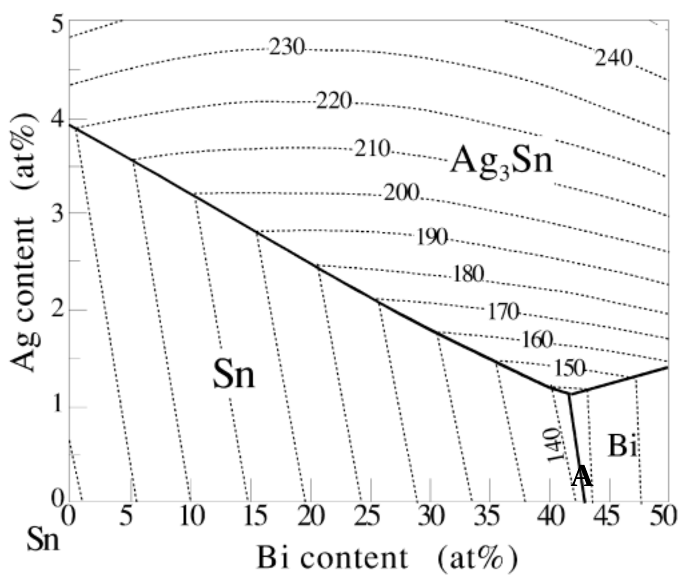

Figure 2.12: Liquidus projection of the Sn-Ag-Bi ternary system (Kattner and Boettinger, 1994)

2.2.2.2 Sn-Ag-Zn Solder

Figure 2.13 shows the Sn-Ag-Zn ternary phase diagram at 190 °C isothermal section. The phase diagram showed that there were Ag-Zn and Ag-Sn binary compounds but no ternary compound has been found. The addition of Zn into Sn-Ag solder reduced the melting point as well as its cost. Since Zn is highly reactive metal, in the liquid state of Sn-Ag-Zn solder, Zn that is exposed to air readily oxidizes. Therefore, even a small amount of Zn can result in the formation of oxide layer at the air-solder interface (Karl, 2004). Furthermore, Zn can also lead to corrosion. However, for this particular ternary system, Ag acts as corrosion resistant, therefore minimize the corrosion-related concern (McCormack et al., 1993). Other than that, addition of Zn also can increase the shear strength of the solder alloys (Luo et al., 2013).

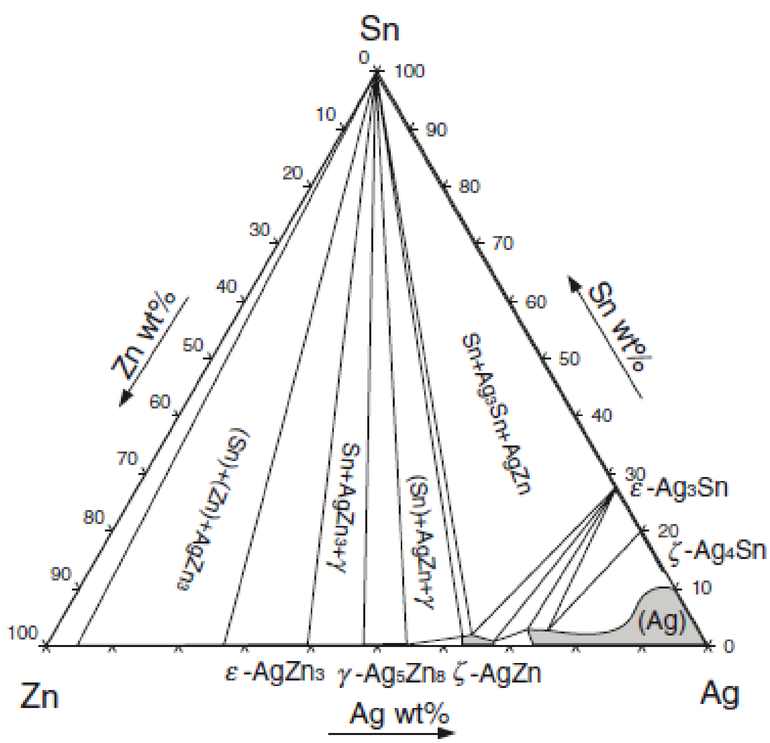

Figure 2.13: Sn-Ag-Zn ternary phase diagram (Chen et al., 2007)