Study on the interconnection failure in lead-free soldered assemblies

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2007

Xu, L. (2007). Study on the interconnection failure in lead-free soldered assemblies.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/5279>

<https://doi.org/10.32657/10356/5279>

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**STUDY ON INTERCONNECTION FAILURE IN
LEAD-FREE SOLDERED ASSEMBLIES**

XU LUHUA

SCHOOL OF MECHANICAL AND AEROSPACE

ENGINEERING

NANYANG TECHNOLOGICAL UNIVERSITY

March 2007

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**School of Mechanical and Aerospace Engineering
Nanyang Technological University**

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

March 2007

ACKNOWLEDGMENTS

I would like to acknowledge and express my earnest appreciation to the following persons:

Associate Professor Pang Hock Lye, John, my dissertation advisor, for his invaluable direction, constant encouragement, and selfless help during this project.

My colleagues in the Electronic Packaging Group, Dr. Che Faxing, Dr. Xiong Bingshou, Mr. Low Tse Hoong, Mr. Sun Yaofeng for their helpful discussion, suggestion, and information.

All the technicians and research students from the CAD/CAM Laboratory, Materials Laboratory A and Strength of Materials Laboratory for their technical supports.

Dr. Shi Xunqing, Mr. Stephen Wong from SIMTech, Prof. Chen Zhong from MSE School, Prof. K.N. Tu from UCLA and Prof. Y. Mutoh from Nagaoka University Technology for their kind help and discussion.

Mr. Chong Desmond from United Test & Assembly Center Ltd (UTAC) for providing FPBGA specimen, Mr. Tan Teck Siong and Shinichi Yoshioka from JEOL Ltd for their support on EPMA analysis.

Finally, I would like to express my gratitude and love to my parents and my wife for their support and dedication.

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ABBREVIATIONS

2D	Two-Dimension
3D	Three-Dimension
AF	Acceleration Factor
Ag	Silver
ALT	Accelerated Life Test
Ar	Argon
AST	Accelerated Stress Test
ATC	Accelerated Thermal Cycling
Au	Gold
BGA	Ball Grid Array
BSE	Back Scattered Electron
CSM	Continuous Stiffness Measurement
CSP	Chip Scale Package
CTE	Coefficient of Thermal Expansion
Cu	Copper
DFR	Design-For-Reliability
DIC	Digital Image Correlation
DISA	Digital Image Speckle Analysis
EDX	Energy Dispersed X-ray
EM	Electromigration
ENIG	Electroless Nickel Immersion Gold (Ni/Au)
EPMA	Electron Probe Micro Analyzer
FC	Flip Chip
FCOB	Flip Chip On Board
FEA	Finite Element Analysis
FPBGA	Fine Pitch Ball Grid Array
FR-4	Fire Retardant class 4 printed circuit board material
iNEMI	International Electronics Manufacturing Initiative
I/O	Input/Output
IC	Integrated Circuit
ICDD	International Centre for Diffraction Data

IMC	Intermetallic Compound
MTTF	Mean Time To Failure
Ni	Nickel
OSP	Organic Solderability Preservative
P	Phosphors
Pb	Lead
PBGA	Plastic Ball Grid Array
PCB	Printed Circuit Board
PQFP	Plastic Quad Flat Package
PWB	Printed Wiring Board
RoHS	Reduction of Hazardous Substances
SAC	Sn-Ag-Cu (e.g. SAC387, Sn3.8Ag0.7Cu)
SEM	Scanning Electron Microscopy
SMA	Surface Mount Assembly
SMD	Solder Mask Definition
SMT	Surface Mounted Technology
Sn	Tin
Sn-Pb	Tin-lead
TC	Thermal Cycling
TS	Thermal Shock
WEEE	Waste Electrical and Electronic Equipment
XRD	X-Ray Diffraction

NOMENCLATURE

C	Concentration of atoms per unit volume
D_0	Diffusion constant
D/kT	atomic mobility
E	Young's (Elastic) modulus (GPa)
E_p	Plastic hardening modulus (GPa)
E_r	Reduced Modulus (GPa)
E	the electric field
e	Electron charge
f	Natural frequency (Hz), deflection (mm)
F	Force (N)
g, G	Acceleration of gravity (9.8m/s ²)
H	Hardness (GPa)
h	Nano Indentation displacement(nm)
I	Moment of inertia
J_{EM}	Atomic Flux by Electromigration (1/cm ²)
j	Current density(A/cm ²)
k	Boltzmann's constant (eV/K)
K	IMC Growth Acceleration Factor
N_f	Fatigue life (cycles)
p	Pressure (Pa)
P	Nano-Indentation Load
$Q, \Delta H$	Activation energy (eV)
R	Electrical resistance (Ω)
T	Absolute temperature (K), transmissibility
t	Time (s), thickness (mm)
t_{eff}	Effective time (s)
t_{eq}	Equivalent time (s)
V	Volume (mm ³), voltage (volts)
V_{EM}	Volume of solder moved by electromigration
ΔT	Temperature range (°C)
η	Characteristic life in Weibull model (cycles)

ν, μ	Poisson's ratio
ρ	Density (kg/m ³), curvature
σ	Normal stress component (MPa)
σ_y	Normal yield stress (MPa)
τ	Shear stress component (MPa)
Ω	Atomic volume
x	IMC thickness
Z^*	Effective charge number of Electromigration

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ABSTRACT

Lead-free solders have replaced tin-lead solders in electronic products due to European Union laws on restriction of hazardous substances such as lead (Pb) since July 1st, 2006. The electronic industry is prepared for lead-free solder reflow manufacturing of electronics assemblies. Solder is the weakest link material in electronic assemblies and it often causes solder joint failures. Hence, lead-free solder joint failure mechanism subject to thermal, mechanical and electrical loadings is studied in this thesis. Solid state IMC growth behavior between 95.5Sn-3.8Ag-0.7Cu solder and Cu-pad or Ni-barrier layer subject to isothermal and thermal cycling (TC) aging was investigated. An integrated IMC growth model as a function of temperature and time for TC aging is proposed. IMC interface failure subject to TC aging was characterized. Mechanical properties of IMC layers and strain-rate dependant properties of solder alloy were characterized by nano-indentation. Electromigration effect on IMC growth behavior and failure at the cathode and anode solder joint interfaces were analyzed. Electromigration-induced back stress and stress gradient were analyzed by studying the movement of nano-indentation marker subject to electrical current induced stressing. The effect of thermal aging on Kirkendall void formation and its subsequent failure mechanism subject to board level impact drop reliability test was investigated.

A comparative study of IMC layer thickness growth by isothermal aging (at 125 °C) versus thermal cycling (-40 to +125 °C) was conducted. The findings were used to develop a framework for correlating IMC layer growth behavior between isothermal and thermal cycling effects. It is shown that the major contribution of IMC growth during thermal shock and thermal cycling aging comes from the high temperature soak

or dwell (125°C) period and this period may be used to estimate the IMC thickness for typical TS and TC aging profiles. Acceleration factor, K, is proposed to correlate the stress effect on IMC growth for TC, TS to isothermal aging at 125 °C. Failure analysis of lead-free solder joints for PBGA assemblies subjected to thermal cycling aging shows that the growth of IMC compounds and the interface crack formation are dependant on solder joint location in the PBGA package. IMC layer thicknesses were measured at different PBGA solder ball locations subject to thermal cycling aging. The highest IMC layer thickness was observed at the outermost solder joint. The thermal deformation generated by CTE mismatch during temperature cycling can affect the IMC growth behavior. Strain concentration at the corner of the solder joint cause thermal fatigue crack growth.

A new approach for applying nanoindentation tests on the planar surface of the IMC layer was developed to determine the elastic modulus and hardness of thin IMC layers (about 1-6 μm) subjected to thermal aging. The IMC composition for NiCuSn ternary IMC during thermal aging was determined by electron probe micro-analysis (EPMA). Elastic modulus of NiCuSn IMC at SAC/ENIG specimen changed from 207 GPa to 146 GPa with different aging time up to 500 hrs. While Cu_6Sn_5 IMC at SAC/Cu specimen remains constant at 97.0 GPa. A constant indentation strain rate ($\dot{h}/h$) characterization method was introduced for hardness measurements. The indentation strain-rate dependant hardness and elastic modulus were measured for strain rates from 10^{-3} to 10 (1/s). The yield stress as a function of strain rate can be estimated from the hardness.

A novel method to measure electromigration (EM) induced back stress was developed by using an array of nano-indentation markers on the cross-section of solder joints. The marker motions driven by a combination of EM and back stress were

measured at different locations, the distribution of back stress, stress gradient and effective charge number Z^* were calculated. The back stress and stress gradient at a neutral plane were measured as 9.01MPa and 97 kPa/ μm , respectively.

The combined sequential reliability test of thermal cycling aging followed by board level drop test for lead-free SnAgCu soldered assemblies were investigated. Significant decrease of drop life was observed for both SAC/ENIG and SAC/Cu-OSP assemblies after thermal cycling aging. Growth of Kirkendall voids and IMC significantly weakened the solder joint interface during TC aging. Drop impact crack path changed from the IMC to the IMC/Cu interface. This work shows that the long-term solder joint reliability subject to thermal aging and drop reliability should be considered.

CHAPTER 1 INTRODUCTION

This introduction chapter provide some background information about lead-free solder joint and failure analysis in microelectronic assemblies. The research objectives, detailed scope of research and outline of the thesis are documented.

1.1 BACKGROUND

The shift to lead-free soldered assemblies in electronic packages incorporates new research knowledge in materials, processes and interconnection failure analysis. This gives rise to new challenges in lead-free manufacturing and reliability problems which have to be solved to ensure successful deployment of lead-free solder and soldering technology. As a joining material, solder provides electrical, thermal and mechanical functions in electronic assemblies. It provides the functional capabilities required for high interconnection density and performance needed in integrated circuits (IC) packages [1-3]. The performance and quality of the solder interconnections depend on the integrity of the solder joints, which are vital to the long-term operation of the electronic assembly. Solder is used in package-level and board-level electronic assembly as shown in Figure 1-1. Solder is the primary means of interconnection for electronic assembly. Lead-free solder for replacing tin-lead solder have been evaluated [4].

Lead-free solders have replaced tin-lead solders due to legislation to ban lead (Pb) usage in electronic products [5-6]. In the European Union (EU), the WEEE and RoHS legislations have taken effect on 1st July 2006. In North America, the National Electronics Manufacturing Initiative (NEMI) organization provides industry with guidelines on lead-free solders and soldering solutions. NEMI recommends lead-free Sn-3.9Ag-0.6Cu solder for soldering reflow process. Characterization of lead-free

solder material properties, manufacturing process implementation and board-level solder joint reliability performance are on-going research areas. Studies on solder joint reliability characterizations of tin-silver-copper (Sn-Ag-Cu) lead-free solder have been reported [7-8]. Materials and mechanical characterization of bulk solder and solder joint properties are needed to better understand lead-free solder and solder joint deformation and failure behavior [9-12]. Thermal aging effects, on IMC growth behavior for lead-based [13] and lead-free [14] solders need further research attention to correlate different thermal cycling aging profiles and isothermal aging effects.

Figure 1-1 Overview of silicon IC assembly process and use of lead-free solder

1.2 RELIABILITY CONCERN OF ELECTRONIC ASSEMBLY

The reliability of a packaged microelectronic system is related to the probability that it will be operational within a service period of time. Electronic assemblies are subjected to thermal aging, mechanical loading, electrical stressing and combined effects of all these loadings in service. Failure mechanisms for electronic solders subjected to these different loadings requires new research efforts. In SMT assemblies, the solder joint in the electronic assembly is often the weakest material link and solder

joint reliability becomes even more important with further minimization of electronic assemblies and its resistance to failure.

Different loadings cause different failure mechanism. For example, thermal cycling test induces high strain cycling and accumulation of visco-plastic deformations in the solder joints. This leads to low cycle fatigue damage in the solder joints. Mechanical shock impact drop test induces brittle fracture failure in the intermetallic layer. Electromigration (EM) at high current density causes faster growth in the IMC and voiding at cathode of the solder joint. Lead-free solder studies on solder joint microstructure, IMC growth, mechanical properties and failure analysis subject to thermal, mechanical and electrical loading are the research challenges investigated and reported in this thesis.

1.3 OBJECTIVE

The objective of this study is to characterize lead-free solder interconnect failure in electronic assemblies subjected to thermal cycling, electromigration, drop impact loading. Combined and sequential effect of thermal aging and electromigration, and thermal cycling aging followed by drop impact loading were investigated.

1.4 SCOPE

The scope of the research work is summarized in the flowchart given in Figure 1-2. It is divided into three parts involving a series of carefully planned tests, specific characterizations and analysis for developing new techniques and models for failure assessments.

Figure 1-2 Flow chart of research work and scope of studies.

The detailed scope of the research work involves six key areas of study:

(1) To characterize the solder joint microstructure, intermetallic compounds (IMC) for Sn-Ag-Cu (SAC) solder joint on copper pad or electroless Ni barrier layer. To measure the IMC growth rate after soldering reflow and subsequent thermal aging exposure. The IMC growth kinetics for lead-free solder interface subject to isothermal and thermal cycling aging was compared for different solder/substrate interfaces. An IMC growth model for thermal cycling aging has not been reported in the literature yet and this is needed to make comparison between isothermal versus thermal cycling

aging research. This can be used to correlate IMC layer growth behavior between isothermal and thermal cycling effects. Hence, a time integrated model is proposed in this thesis to predict the IMC growth for different thermal cycling aging profiles as a function of temperature and time. Thermal cycling induced stress-strain effect on IMC growth was demonstrated by comparing IMC growth behavior for thermal shock, thermal cycling and isothermal aging experiments.

(2) To characterize the mechanical properties of IMC layers, SAC solder alloy, metallization and the substrates before and after thermal aging by nano-indentation continuous stiffness measurement (CSM). A new approach for nano-indentation of thin IMC layers in actual solder joint from the planar IMC surface was investigated.

(3) To characterize the strain-rate dependant mechanical properties of the SAC solder. The indentation strain-rate dependant hardness and elastic modulus were investigated measured for 0.001, 0.01, 0.1, 1 and 10 (1/s), respectively.

(4) To characterize the failure mechanism of SAC solder joints in PBGA assemblies subjected to thermal cycling aging. The growth of interfacial IMC compounds and the interfacial Kirkendall voids formation subject to thermal cycling aging were investigated.

(5) To characterize EM-induced IMC growth in solder joints at the anode and cathode interfaces. A method for characterizing the EM-induced back stress, stress gradient in a solder joint was introduced. An experiment for demonstrating the EM induced back stress effect on atom transport movement was studied by tracking the movement of nano-indentation markers on the cross-section of a solder joint. The marker motions driven by combination of electrical flow and back stress effects was investigated.

(6) To study the combined sequential effects of thermal aging exposure followed

by mechanical drop impact loading on solder joint reliability. Thermal cycling aging followed by board level drop reliability test was investigated. Lead-free SAC in FPBGA packages mounted on PCB with Cu-OSP and ENIG surface finish were aged for 500, 1000 and 1500 thermal cycles, respectively. Drop impact failure lifetime before and TC aging were compared and the impact failure mechanism was investigated.

1.5 OUTLINE OF THE THESIS

This thesis is organized into eight chapters. Chapter 1 and 2 are the introduction and literature review chapters. Chapter 3 to Chapter 7 are the main parts of this thesis, each part includes individual illustration of experiments, results, discussion and summary. Chapter 8 is the conclusions. Details of sample preparation, necessary description of experimental setup and publications are given in the appendix (I, II and III).

CHAPTER 2 LITERATURE REVIEW

In this section, previous reported work in the literature related to the Sn-Ag-Cu (SAC) lead-free solder, solder interfacial reactions, IMC growth models and properties characterization, electromigration and its effects on solder joint reliability have been reviewed.

2.1 SN-AG-CU SOLDER PROPERTIES

There are strict performance requirements for solder alloys used in microelectronic assemblies. In general, the solder alloy must meet the expected levels of electrical and mechanical performance, and must also have the desired melting temperature for soldering process control. It must adequately promote good wetting on PCB pads, and provide reliable solder joints under service conditions.

The lead-free solder to replace tin-lead (Sn-Pb) solder must be comparable to or superior than Sn-Pb solders in mechanical properties. The major performance characteristics of lead-free solders for board assembly are manufacturability, reliability and environmental suitability. Manufacturability describes how well a lead-free solder fits into current second level packaging practices without requiring significant changes. Manufacturability involves most of the physical properties of a solder alloy relevant to soldering such as melting temperature, solderability, viscosity, density, thermal and electrical properties, corrosion and oxidation behavior, surface tension, reworkability and cost. Reliability of a solder joint for the first and second level packaging is dependent on careful selection of materials and its properties such as the coefficient of thermal expansion, elastic modulus, yield strength, shear strength, fatigue and creep behavior of the solder alloy. The properties of solders that are of importance from a manufacturing and reliability standpoint of view are summarized in Table 2-1 [15].

Table 2-1 Important properties of solder alloys

Properties relevant to manufacturing	Properties relevant to reliability and performance
Melting/liquidus temperature	Electrical conductivity
Wettability (of pad)	Thermal conductivity
Manufacturability using current processes	Coefficient of thermal expansion
Ability to be made into balls	Shear properties
Ability to be made into paste	Tensile properties
	Creep resistance
	Fatigue properties
	Intermetallic compound formation

2.1.1 Comparison between Sn-Pb and SAC

For the application of solder in surface mount technology (SMT), the major difference between eutectic Sn-Pb solder and SAC solder are their melting temperature, wetting behavior and mechanical properties [16]. The melting point of eutectic 63Sn37Pb solder is 183 °C, and the peak temperature during reflow process is normally 215-230°C. However, SAC solder, Sn-(3-4)Ag-(0.5-0.7)Cu, has a much higher melting point of 217 °C; this means that the peak temperature of reflowing profile has to around 235-260°C. The higher soldering temperature presents a serious concern on the suitability of polymeric materials used previously in packaging. The solder joint and IMC stability and reliability subject to thermal, electrical and mechanical loading is another major concern.

2.1.2 Microstructure Effect on Mechanical Properties

The microstructure of SAC solder comprises of Sn-rich matrix with dispersed IMC particles of Ag_3Sn , Cu_6Sn_5 , which provide improved mechanical properties in the bulk solder. Sn-rich phase has the body-centered tetragonal lattice structure and tends to deform by twinning [17-18]. The difference of the mechanical properties between eutectic Sn-Pb solder and SAC can affect the reliability level and failure expectation of

solder joints. The tensile properties, shear properties, creep and fatigue properties are dependent of temperature and microstructure. Both Sn-Pb and SAC solder are viscoplastic materials and their mechanical properties are strain-rate-dependent as well [15, 19].

Tensile properties

Tensile properties such as yield strength, ultimate tensile strength and ductility (elongation in %) can be expected to be microstructure and dependent of strain rate. The microstructure in turn depends on chemical composition and thermal history, including cooling rate and aging. Since solder alloys operate at high homologous temperatures (0.5 to 0.8 T_m , melting temperature), thermal aging over the lifetime of the electronic system is expected. Hence, characterization of the change in strength after aging conditions is need. It is also important that the experimental strain rate reflect the strain rate in microelectronics assemblies. Pang and Xiong et al. [11, 20-21] showed that Sn-0.7Cu and Sn-3.8Ag-0.7Cu lead-free solder types have superior tensile properties to Sn37Pb eutectic solder. The Ultimate Tensile Strength (UTS) are strongly related to microstructure, strain rate, and temperature. For example, SAC solder has elastic modulus and yield stress of 50 GPa, 40MPa, respectively, at room temperature with a strain rate of 5×10^{-3} 1/s. While for Sn37Pb solder, it has a modulus of 30GPa and yield stress of 20 MPa correspondingly.

Shear properties

Solder joints in microelectronics systems experience the shear loading due to CTE mismatch deformations. The shear properties, namely the shear modulus and shear strength are dependent on the strain rate and test temperature. The shear strength decreases at lower strain rates or higher test temperatures, with the temperature effect being the primary effect and the strain rate for secondary effect [21].

Fatigue

Isothermal low cycle fatigue test imposes cyclic constant strain at different isothermal temperatures. Thermal fatigue, resulting from temperature cycling test has severe strain changes resulting from dissimilar thermal expansion and bending warpage deformations. Fatigue in solder joints leads to crack initiation and propagation. The fatigue life of a solder joint is determined by the damage accumulated per cycle [22]. The cyclic stresses and strains are well below the yield stress or strain of the material. Fatigue failure can occur due to defects and irregularities in the microstructure in progressive growth of crack from these defects. One way of enhancing the fatigue life of a material is by altering its resistance to crack initiation or crack propagation. Failure in solder alloys involves both fatigue and creep behavior [23-25]. For eutectic tin-lead solder, it is important to study the failure mode in creep and in fatigue. As solders are increasingly expected to perform in a very dynamic service environment where strain distributions change with time, the capability to understand the fatigue resistance behavior of lead-free solders is very important [26-30].

2.2 INTERMETALLIC SYSTEM IN SN-AG-CU SOLDER

In the molten solder, metallurgical reaction between solder and interconnection pad materials (Cu, Au, or Ni) is inevitable and forms layers of intermetallic compound (IMC) at the solder and metallization interface [31-34]. The thickness of this IMC layer is important as the IMC is brittle. The thickness of the IMC layer depends on factors like temperature of the molten solder and holding time. A suitable holding time and a high temperature are necessary for reflow of surface mount assemblies onto the PCB to form strong solder joints. This combination could lead to a fairly thick IMC layer at the solder and metallization interface. An optimal thin layer of IMC with good wetting gives a mechanically stronger solder joint. Compared to a thick IMC layer

which leads to embrittlement of the solder joint [35]. Since the thickness of the metallization layer is thin, a long holding time could also result in over consumption of metallization layer resulting in de-bonding of the joint. Therefore, it is important to control the growth of IMC layer thickness and the consumption rate of metallization layer for long term solder joint reliability performance.

2.3 IMC GROWTH KINETIC ANALYSIS

2.3.1 Solder Joints in Service Conditions

IC packages with high-density interconnections generate heat during service and the heat is dissipated through the leads, solders bumps. The temperature increase due to this heat generated is enough to activate the diffusion of elements across the solder joint interface. As a result, the IMC layer grows in thickness. Because of the difference in coefficient of thermal expansion (CTE) of the interconnect materials thermal strains are developed in the joint. The brittle nature of IMC causes failure at low stress and strains. Mechanical failure of solder joints also results from vibration or shock loading caused during transportation and usage. As the strength of the solder joint may correlate with IMC layer thickness, the long-term reliability of the solder joint could depend on the growth kinetics of the IMC layer during service. Hence, it is important to analyse growth kinetics of the IMC layer to assess the long-term reliability of the solder joint. Solder joints experience thermal fatigue due to temperature fluctuations during power on/off or environment induced temperature cycles. IMC layer growth takes place during in-service condition. The growth kinetic analysis is usually carried out isothermally at various elevated temperatures. Thermal cycling behaviour could accelerate IMC growth due to the combination of temperature and cyclic stress-strain loading conditions [36-39].

2.3.2 Solid State Reaction

Fundamental studies on growth kinetics of IMC layer in solid state between Cu and Sn-Pb solder alloys are generally carried out on Cu-solder diffusion couples. A lot of work has been done on the solid state reaction at the substrate/solder interface during isothermal annealing [40-50]. They are prepared by melting and solidifying solder alloys on Cu, during which a thin layer of η -phase or ε -phase, or both phases are formed at the interface depending on the soldering conditions. These IMC layers grow with time upon isothermal annealing because of the diffusion of Cu and Sn in the existing IMC layer. The thickness of IMC layer formed during the preparation of diffusion couple, the as-soldered thickness x_0 is subtracted from the thickness x at any given time, to determine the growth rate. The IMC growth model can be expressed as,

$$x = x_0 + A_0 t^n \exp(-\Delta H / RT) \quad (2-1)$$

A_0 is pre-exponential constant, n the time exponent, ΔH the apparent activation energy for the growth, R the gas constant (8.314 J/K•mol) and T the absolute temperature. It must be noted that the equation (2-1) is an empirical relationship. The different initial IMC thickness x_0 will lead to different subsequent thickness growth rate, for example, if x_0 equals to 0.5 microns or 5 microns, the growth rate during thermal aging is obviously different, thus the constant A will be dependant on the initial condition, and the time exponent may vary. But for very small initial IMC thickness of 0.5 to 1.0 μm this equation is applicable.

There are also reports of experimental determination of n values. Tu and Thompson [15, 49] showed that η -phase grew linearly with time ($n = 1$) in a Cu-Sn thin film diffusion couple upon annealing at room temperature. After consuming all the Sn in the Cu-Sn diffusion couple, it became a diffusion couple of Cu and the η -phase. This diffusion couple was further annealed at higher temperatures (between 115°C and

150°C) and the results showed that the η -phase layer (Cu_6Sn_5) thickness decreased with square root of time while forming the ε -phase layer (Cu_3Sn) at the Cu/ η -phase interface. In other words, the ε -phase layer grew with square root of time ($n = 0.5$). Their experiment also shows that the growth rate of η -phase at room temperature decreases with increase in thickness of the Sn film.

2.3.3 Growth Mechanisms

The growth of IMC layer requires the diffusion of Cu and/or Sn in the existing IMC layer to various interfaces for the reaction to occur. When there is more than one layer of intermetallics, their growth requires a complex combination of several mechanisms. The n and ΔH values obtained experimentally correspond to the particular controlling mechanism. For each value of n obtained from power law fitting, there is a proposed growth mechanism. These growth mechanisms are derived from the existing theory on diffusion. For example, if a value of $n = 0.5$ is obtained, then the controlling mechanism is thought to be the lattice diffusion. Similarly, if $n = 1.0$, the IMC growth is controlled by interface reaction. However, there are other mechanisms that could control the process whose n values are deduced to be different to 0.5 and 1.0. The grain boundary diffusion controlled mechanism is proposed for values of $n = 0.4$ and $n = 0.25$ [48, 50]. For $n = 0.33$, a mechanism similar to grain ripening was also proposed [51-53].

2.3.4 Effect of Microstructure on Growth of IMC

The microstructure of the IMC layer has a great influence on the growth kinetics. The non-parabolic growth kinetics is due to the presence of large amount of grain boundaries in IMC layer. The presence of grain boundaries accelerates the growth rate of the IMC layer as shown by Bader *et al* [54]. They reported that the IMC growth rate is almost two times faster in thin polycrystalline films compared to that in the single

crystals of Cu and Ni layers. The absence of grain boundaries in single crystal layer caused lower IMC growth rate compared to the thin film samples as the elements diffuse faster through grain boundaries than through the grains [55].

2.3.5 Thermal cycling

Thermal cycling or thermo-mechanical fatigue testing of solder joints is important for characterizing the reliability of the solder joint. The formation of brittle IMC layers, are inevitable and can affect the long-term solder joints reliability. In service, the components undergo thermal cycling during each power switch on/off cycle. Because of large difference in the coefficient of thermal expansion of the different constituents of the package assembly, and locally in the solder joints (the under bump metallization layer, IMCs and solder alloy), stresses are developed in the joint which will eventually lead to the failure of the joint. Thermal cycling of joints also leads to degradation of joint strength, which is proportional to the number of cycles [56-57]. Pang *et al* [10] reported that the fatigue life of single solder joint specimen-63Sn37Pb solder ball of 0.5 mm diameter soldered between two layers of Cu pad-decreased after it was subjected to thermal cycling ageing between -40°C to 125°C with 15 mins dwell time at the extreme temperatures. The fatigue strength was reduced by about 6 times after 1000 cycles and 8 times after the next 1000 cycles. Harrison *et al* [56] and Stam and Davitt [57] also showed that the shear strength decreases after thermal cycling in various substrate-solder combinations.

The growth kinetic analysis of IMCs due to thermal cycling has not been adequately reported in the literature. Most of the reported work concentrates on the microstructural changes in the solder like coarsening of the secondary particles, redistribution of these particles typically found in SAC solders. Thermal cycling studies are focused on determining the number of cycles to failure in the given temperature

range. Under thermal cycling, the IMC layer growth kinetic analysis is not as simple as the case for isothermal annealing because the IMC growth kinetics is dependent of temperature and time during the thermal cycle. The function of temperature and time must be integrated for the calculation of IMC growth subject to non-isothermal aging condition.

Marshall and Walter [58] reported that the IMC layer thickness at the Cu-pad and Sn-5Ag solder interface increased from 1 micron to 3 microns after 700 cycles (temperature range is -30°C to $+100^{\circ}\text{C}$ with 60 mins dwells and ramp rate of 6.5 K/min). This increase in IMC layer thickness is less compared to the increase in IMC thickness (less than 1 micron to 5 micron) by isothermal annealing at 100°C for the same time (about 75 days) as reported by Zakraysek [59]. Choi et al [60] compared the IMC layer thickness at the interface between Cu/electroless Ni/evaporated Au layers on FR4 PCB and five lead-free solders (Sn3.5Ag6.5In , Sn3.5Ag0.5Cu , Sn3.5Ag1.0Cu , Sn3.5Ag1.5Cu and Sn3.5Ag0.5Ni) when subjected to thermal cycling (-65°C to 150°C , 10 min dwell time) for 100 cycles and isothermal annealing at 130°C for 400 hours. They found that the IMC layer thickness is smaller in thermal cycled samples compared to isothermally annealed samples in all joints except the joint containing indium. It is noted that the peak temperature in thermal cycling is higher than the isothermal temperature. However, this is not directly comparable since the IMC growth may not be significant at the low soak temperature, and there is no criterion for correlating isothermal aging IMC growth with thermal cycling aging IMC growth.

Vianco et al [13] studied the isothermal and thermal cycling aging behaviour of $63\text{Sn}37\text{Pb}/\text{Au-Pt-Pd}$ thick film couples. They have proposed an empirical relationship to find out the “effective annealing time”, which is defined as one-half of the total thermal cycling time, at equivalent isothermal annealing temperature corresponding to

the thermal cycling temperature range. This equation is derived from the growth kinetic analysis of isothermally annealed specimens and requires the thickness of IMC layer after thermal cycling. The empirical relationship to compute the IMC layer thickness between the 76Au21Pt3Pd metallization and 63Sn37Pb solder joints is given by equation (2-2),

$$x = 0.93 + 0.0134t^{0.78 \pm 0.8} \exp\left(-\frac{\Delta H}{RT}\right) \quad (2-2)$$

where $\Delta H = 106 \pm 8$ kJ/mol. The equivalent temperature is computed using Eqn. 2-2 for the measured thickness of IMC layer and the effective annealing time. For example, if a thickness is measured after 400 thermal cycles in the temperature range of -55°C to +125°C with a dwell time 30 min and ramp rate 6°C/min, the same thickness of IMC layer can be expected when the joint was annealed isothermally at $127 \pm 3^\circ\text{C}$ for 400 hours (16.7 days). Note that the equivalent temperature is slightly higher than the peak temperature in thermal cycling.

Vianco et al have also shown that the equivalent temperature increases in thermal shock treatment. The equivalent temperature is $134 \pm 2^\circ\text{C}$ for 400 cycles of thermal shock in the temperature range -55°C to 125°C with a dwell time 10 min. An accelerated growth rates for thermal cycling and thermal shock aging was noted when compared to isothermal annealing. The proposed reason for this growth is the internal stress-strain effect developed due to CTE mismatch. Vianco et al's method gives some insight into the growth kinetic analysis of IMCs in thermal cycled treatment. It will be useful to develop IMC growth model subject to thermal cycling or non-isothermal aging. This is reasonable as the growth mechanism for thermal cycling should be related to isothermal aging. The growth parameter obtained from isothermal aging can help to determine the non-isothermal aging IMC growth model.

2.4 CHARACTERIZATION OF IMC PROPERTIES

2.4.1 IMC Properties

SAC solder reflowed with Cu or Electroless Nickel / Immersion Gold (ENIG) surface finish generates intermetallic compound (IMC) layers, such as Cu_6Sn_5 , Cu_3Sn , Ni_3Sn_4 and Cu-Ni-Sn ternary phase. One of the major reliability concerns is the brittle nature of the IMCs and the subsequent IMC growth subject to solid state thermal aging. The mechanical properties of the IMCs were reported in previous studies [61-64]. In recent nano-indentation studies[65, 66], the modulus, hardness and yield strength of solder joints were reported. For SAC/Cu reaction couple, long time aging at high temperature or longer reflow time were used to obtain a thick Cu_6Sn_5 and Cu_3Sn IMC layer at least about 20 μm , this is to meet suitable IMC layer thickness requirements for nano-indentation tests on cross-sectioned specimens. However, this type of IMC specimen prepared in laboratory is not representative of actual solder joints formed by reflow. For example, SAC solder joint reflowed on electroless nickel and immersion gold(ENIG) surface finish has a Ni layer of 3-5 μm thick and an IMC layer of less than 1 μm thick. It is not possible to generate a thick NiCuSn IMC layer for cross-section measurements. Furthermore, long-time reflow or aging for SAC/ENIG solder joint may affect the IMC composition, grain size and crystal orientation during IMC growth. Thus their mechanical properties are subject to changes, for example, in SnAgCu/Ni couple, the IMC formed on the interface is Ni-Cu-Sn ternary phase, the change of ratio between Cu and Ni may generate different IMC, $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$ or $(\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4$ [67]. The value of x and y can vary from 0 to 0.5, and the exact value can be measured for an individual IMC crystal structure by electron probe micro analysis(EPMA).

2.4.2 Nano-indentation Measurement

Nano-indentation is a useful test to determine the hardness and modulus of the

materials involved in solder joint. However, the reliability of the results depends on the observance of special measurement conditions and the elimination of undesired influences such as creep induced deformations. It is known that a creep-induced depth increase arises in Sn phase when the load is held constant after having reached the maximum load. This is expected as solder creeps even at room temperature. The depth changing rate may reach several nanometers per second at the beginning of the hold period. Furthermore, this creep behavior not only influences the maximum depth but also the gradient of the upper part of the unloading curve which is used for the calculation of contact stiffness and modulus. The depth will continue to increase if the unloading rate is low, and thus the contact stiffness and modulus measurement become distorted.

Continuous Stiffness Measurement (CSM) offers a significant improvement in nano-indentation testing. CSM is accomplished by imposing a small, sinusoidally varying signal on top of a DC signal that drives the motion of the indenter [68]. This allows the measurement of contact stiffness at any point along the loading curve and not just at the point of unloading as conventional measurement. It makes the continuous measurement of modulus possible in one sample experiment without the need for discrete unloading cycles. The significance of CSM technique in measuring IMC and solder is that, firstly, modulus is given once the indentation start and the value tend to be stable after 50-100 nm. Operators can get result at exceedingly small penetration depth and test can be conducted on thin IMC layers or particles. Secondly, the effect of creep behavior for solder could be removed from the measurement since the oscillating force coupled with DC signal only generates small elastic displacement.

The calculation of elastic modulus and hardness for nano-indentation CSM was based on the Oliver and Pharr Method [69]. The difference between the CSM and

conventional method is how contact stiffness was obtained. At every oscillating cycle imposed in CSM, contact stiffness S was measured while the linear load increases. The fundamental relations of hardness H , reduced elastic modulus E_r and contact stiffness are given in equation (2-3) and (2-4).

$$H = P / A \quad (2-3)$$

$$E_r = \sqrt{\frac{\pi}{2\beta}} \frac{S}{\sqrt{A}} \quad (2-4)$$

where P is the load and A is the projected contact area at that load. E_r is the reduced elastic modulus and β is a constant that depends on the geometry of the indenter ($\beta=1.034$ for a Berkovich indenter). S is the contact stiffness.

The true elastic modulus E for the tested IMC layer could be calculated from the reduced modulus E_r , as given in Equation (2-5).

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (2-5)$$

where the ν is the Poisson's ratio for the IMC layer, E_i and ν_i are the elastic modulus and Poisson's ratio of the indenter tip. For diamond tip, $E_i=1141\text{GPa}$ and $\nu_i=0.07$ [68].

The projected contact area A is a function of contact depth h_c , for Berkovich tip, Equation (2-6) and (2-7) give the calculation of h_c and A .

$$h_c = h - \varepsilon \frac{P}{S} \quad (2-6)$$

$$A = 24.56h_c^2 \quad (2-7)$$

The major difference between CSM technique and conventional method is the way in determine the contact stiffness S . For conventional nano-indentation, stiffness is the differentiation of load over penetration at the maximum depth of the unloading curve,

as given in Equation (2-8).

$$S = \left(\frac{dP}{dh} \right)_{h=h_{\max}} \quad (2-8)$$

For CSM, stiffness is determined by the harmonic oscillating force $P_h = P_{os} \exp(i\omega t)$ and the displacement response of the indenter $h(\omega) = h_0 \exp(i\omega t + \varphi)$ added to the nominally increasing load, P , on the indenter. As given in Equation (2-9).

$$S = \left[\frac{1}{\frac{P_{os} \cos \phi}{h(\omega)} - (K_s - m\omega^2)} - K_f^{-1} \right]^{-1} \quad (2-9)$$

where P_{os} is the magnitude of the force oscillation, $h(\omega)$ is the magnitude of the resulting displacement oscillation, ω is the frequency of the oscillation and φ is the phase angle between the force and displacement. K_s , K_f and m are the equipment parameters, stiffness of spring that support indenter, stiffness of frame and mass of the indenter, respectively. The contact stiffness was measured continuously while the indenter tip penetrates into the surface. The elastic modulus was then determined by Eq(2-4) and Eq(2-5).

It should be noted that contact stiffness is related to the contact depth h_c . The relationship between them can be determined from Eqn (2-4). For a perfect Berkovich indenter, A is a function of contact depth h_c , as shown in Eq. (2-7). Substituting Eq. (2-7) and value of π , β into Eq. (2-4), one obtains Eqn (2-10) and Eqn (2-11).

$$E_r = 0.2487 \frac{S}{h_c} \quad (2-10)$$

$$S = 4.021 E_r h_c \quad (2-11)$$

Since reduced modulus E_r is a constant for a uniform material, contact stiffness S is linearly proportional to h_c . But for non-uniform materials, such as thin IMC layer over substrate, measured E_r will be affected by substrate when penetration depth exceeds 15%

thickness of IMC layer. $S-h_c$ curve will not be a straight line anymore. By analyzing the change of $S-h_c$ slope, we can determine which part should be selected for calculation of modulus.

2.5 SOLDER JOINT RELIABILITY TESTS

Reliability tests of electronic assemblies are very important concerns to ensure long-term reliability of electronic products. In service, electronic products failures can occur within a year but often much longer. Therefore, it is not practical to test at service load level and it is uneconomical with respect to test time and cost. Accelerated life testing (ALT) methods are employed for the purpose of accelerating reliability test results.

Reliability tests aim at revealing and understanding the physics of failure. Another objective of reliability tests is to accumulate representative failure statistics [70]. Accelerated tests use elevated stress levels and/or higher stress-cycle frequency to precipitate failures over a much shorter time. Stress loading includes constant stress, step stress, progressive stress and random stress [71]. Typical accelerating stresses are temperature, mechanical load, thermal cycling or thermal shock, cyclic bend, drop impact and vibration. Such tests can facilitate physics of failure for reliability tests that cost effectively, shorten the product process and improve long-term product reliability.

Accelerated tests can be performed at any level, such as part level, component level, board level, equipment level and system level. The degree of stress acceleration is usually determined by an acceleration factor. This factor is defined as the ratio of lifetime under normal service conditions to the lifetime under accelerated conditions.

2.5.1 Accelerated Thermal Cycling (ATC)

When accelerated thermal cycling (ATC) tests were carried out, the acceleration factor (AF) given by Norris and Landzberg [72] has been used to relate test conditions

to field conditions for lead based solder joint reliability:

$$AF = \left(\frac{\Delta T_t}{\Delta T_f} \right)^{1.9} \left(\frac{f_f}{f_t} \right)^{1/3} \exp \left[1414 \left(\frac{1}{T_{\max.f}} - \frac{1}{T_{\max.t}} \right) \right] \quad (2-12)$$

where $\Delta T_t, \Delta T_f$ are temperature ranges at test and field conditions; f_t, f_f are the cyclic frequencies at test and field conditions; $T_{\max.t}, T_{\max.f}$ are the highest temperature in K at test and field conditions, respectively. When the accelerated factor, AF , is determined and reliability test data are known, the life distribution, reliability function, and failure rate for field condition can be calculated using best-fit Weibull life distribution model considering linear acceleration case in which the Weibull plots of the field condition and testing condition have the same Weibull slope [73]:

$$F_f(x_f) = 1 - \exp\left(-\left(x_f / AF \cdot \theta_t\right)^{\beta_t}\right) \quad (2-13)$$

$$R_f(x_f) = \exp\left(-\left(x_f / AF \cdot \theta_t\right)^{\beta_t}\right) \quad (2-14)$$

$$h_f(x_f) = (\beta_t / AF \cdot \theta_t) \left(x_f / AF \cdot \theta_t\right)^{\beta_t-1} \quad (2-15)$$

where x_f, F_f, R_f , and h_f are time-to-failure, life distribution, reliability function and failure rate at field condition, respectively, β_t, θ_t are shape parameter and characteristic life at testing condition, respectively, and AF is accelerated factor.

The two common ATC tests for solder joint reliability used in industry are the thermal cycling (TC) [74] and thermal shock (TS) [75] tests. TC has a ramp rate varying from 8°C/min to 33°C/min, whereas TS condition has a ramp rate between 33°C/min and 55°C/min. Dwell time is included at the cycle extremes to allow for creep and stress relaxation process to take place. Different temperature ranges are shown in Table 2-2 for different service environments for electronic products.

Table 2-2 Thermal environments for electronic products

Use condition	Temperature range (°C)
Consumer electronics	0 to 60
Telecommunications	-40 to 85
Commercial aircraft	-55 to 95
Military aircraft	-55 to 125
Space	-40 to 85
Automotive-passenger	-55 to 65
Automotive-under the hood	-55 to 150

2.5.2 Board Level Drop Impact

Reliability testing of soldered assemblies subjected to drop impact is critical, especially for handheld or portable telecommunication devices such as mobile phone and Personal Digital Assistant (PDA) because these products are prone to accidental drop resulting in failure. Drop tests are increasingly required for personal electronic products. There are mainly three types of drop tests in the electronic industry: (a) free fall product level; (b) free fall board level; and (c) controlled pulse drop at board level. Board level drop test is convenient to characterize the solder joint performance, as it is more controllable than product level drop test. Some researchers had conducted board level drop tests to understand the response of solder joint to impact loading using different boundary conditions such as 4 or 6 screw support [76, 77], clamped-clamped boundary condition [78, 79] and free fall drop [80, 81]. Some researchers [82, 83] had conducted product level drop tests due to real drop events. The maximum acceleration of PCB can reach to more than 1000G when subjected to drop impact, but the displacement and strain of the PCB is relatively small. Suhir [84] stated that it is dynamic stress, not the acceleration, which is a true criterion of the dynamic strength.

Keltie and Falter [85] proposed an approximate method to simulate different parameters effects, such as mass ratio, stiffness ratio, pulse width ratio, and rotational stiffness ratio, on response analysis of electronic assemblies using a simple structure consisting of a mass attached to a beam.

Lead-free solder usually exhibits less drop impact life than lead-based solder from many test results. Amagai et al. [86, 87] proposed that the number of drop to failure decreased with Ag content increasing for SnAgCu solder and the drop failure performance could be improved by adding some optimum Indium and Nickel to SAC solder.

2.5.3 Electromigration

As the size of the solder joint decrease, the current density the solder joint endure will be higher. Brandenburg and Yeh [88] reported the electromigration failure in flip chip eutectic Sn-Pb solder joints of 125 μm in diameter, stressed under $8 \times 10^3 \text{ A/cm}^2$ at 150 $^\circ\text{C}$ for a few hundred hours. The key observations are void formation at the cathode and Pb accumulation at the anode of the solder joint. The parameters in the mean-time-to-failure (MTTF) equation (Black's equations) were determined, and the equation was given as equation (2-16)

$$MTTF = AJ^{-n} \exp\left(\frac{-\Delta H}{kT}\right) \quad (2-16)$$

where the pre-factor $A=0.8$, the current density J has a power factor of $n=1.82$, the activation energy $\Delta H=0.8 \text{ eV/atom}$, k is the Boltzman constant and T is the temperature (K). The equation was used to project electromigration failure for flip chip solder joints and showed that electromigration in solder joints was of real concern for flip chip technology.

A schematic diagram of the test structure is shown in Figure 2-1. The failure

mechanism has been assumed to be the void nucleation and spreads rapidly across the contact due to the current crowding [89]. The electromigration failure behavior was monitored by resistance change and the failure mode was examined by cross-sectional SEM. The result shows that there was a long incubation time with very little resistance change. Beyond that a rapid change occurred.

Figure 2-1 A schematic illustration of the mode of electromigration test and failure in a flip chip solder joint. [89]

Normally, atomic flux divergence occurs near the upper-left edge, where the electrons enter the bump. It leads to vacancy accumulation. As a void nucleates by condensing the super-saturated vacancies, it will displace the current to its surrounding area and leads to a lateral growth of the void. So, the void spreads across the contact and finally failure occurs. At the same time, Pb accumulation was observed in the opposite side of the joint, the anode side.

For electromigration consideration, the design rule in electronic packaging is to distribute 1 A over five solder bumps, or 0.2 A per bump. For a solder bump of 50 μm in diameter, the current density will be about $3 \times 10^3 \text{ A/cm}^2$. Since the contact area of the bump is much smaller than the cross-section of the bump, the actual current density will reach about 10^4 A/cm^2 in the solder bump contact. While this current density is about one to two orders of magnitude less than that in Al or Cu interconnects lines [89-92], electromigration in the solder bumps cannot be ignored. The first reason is because

of the low melting point and high atomic diffusivity of solder alloys. For the eutectic Sn-Pb solder with a melting point of 183 °C, room temperature is two-thirds of its melting point in absolute temperature scale. At room temperature, it is known that cellular precipitation occurs in Sn-Pb alloys, Sn whiskers grow on Sn surface finish, and microstructure coarsening takes place in eutectic Sn-Pb. The room temperature self-diffusivity in eutectic SnPb lamellar interface is about 10^{-8} cm²/s.

The second reason is because of the large current density change between the interconnect line and solder bump due to geometry change at their interface. In conducting the same current, the current density change will be two to three orders of magnitude from the line to the solder bump. Hence, a large current crowding occurs at the interface. Since the interface is also a divergent plane of atomic diffusion, it becomes the failure site of electromigration [93,94].

2.5.4 Combined Effect of Sequential Loading

Reliability test that combines more than one loading or sequential loadings are rarely reported in literature. The difficulty of assessing combined effects of sequential testing is that the failure mechanism is more complicated to analyze. The interaction between different effects of sequential loading is challenging research areas. For example, thermal cycling aging followed by drop impact is a representative case that occurs in actual solder joint (See Table 2-3). Another example is the concurrent of thermal diffusion and electromigration, which is caused by high current density and the Joule heating effect.

Table 2-3 Combined sequential testing and possible failure mechanism

Combined Testing Method	Possible Failure Mechanism	Practical Background
Concurrent thermal diffusion and electromigration	IMC growth and void growth	Power on and high soak temperature
Thermal cycling-drop impact	TC-induced interface crack lead to earlier drop failure	portable electronics drop impact after TC

CHAPTER 3 SOLDER JOINT MICROSTRUCTURE AND IMC

The major difference between eutectic Sn-Pb solder and Sn-Ag-Cu (SAC) solder are their melting temperature [95]. The melting point of eutectic Sn-37Pb solder is 183 °C, while SAC eutectic solder has a much higher melting point of 217 °C. The microstructure of the SAC solder has a mixture of Sn-rich matrix and IMC particles. In this section, the microstructure of the SAC solder joint was characterized. The morphology for the two major intermetallics (IMC), Ag₃Sn and Cu₆Sn₅, which formed in the solder matrix, were investigated. The interfacial IMCs in 95.5Sn-3.8Ag-0.7Cu/Cu-pad and 95.5Sn-3.8Ag-0.7Cu/ENIG barrier layer solder joint were observed to give better understanding of the initial condition for aging studies in the followed chapters.

3.1 EXPERIMENTAL PROCEDURES

Solder droplet specimens and single BGA solder joint specimens were used to study the growth of IMC subject to isothermal and thermal cycling aging experiment. The reflow process was done using the 8-zone reflow oven. The increasing temperature in the oven activates the flux. It must then keep the surfaces deoxidized until the wetting of the solder. The specimens were placed on the reflow machine belt and subject to the reflow temperature profile. The belt speed was set as 50 cm/min, the reflow time above the melting point 217 °C was 120 seconds. The reflow peak temperature was 250 °C. Different belt speeds 10, 30, 50, 70, 90, 110 cm/min were used for comparison, the reflow time above 217 °C were 600, 200, 120, 86, 67 and 54 seconds, respectively. (See Appendix I for further details on the fabrication of samples).

The temperature is measured and recorded by a sensor fixed near the soldering specimen; the temperature profile is then read out to computer, the profile is finally

optimized to the required condition by adjusting the heaters (see Table 3-1). The reflow process can be characterized with four different phases: Preheat, Thermal Soak, Reflow and Cool Down. Metallurgical reaction between solder and interconnect materials Ni/Au is inevitable and it forms layers of intermetallic compound (IMC) at the solder/metallization interface. The thickness of this IMC layer is a key factor because the IMC is brittle, in addressing the reliability and life-time prediction of the solder joint. The thickness of the IMC layer depends on factors like temperature of the molten solder and holding time. A long holding time and a high temperature can generate more IMCs.

Table 3- 1 Temperature setting of the heating zones

Zones	1	2	3	4	5	6	7	8	9	10
Heating temperature	100	140	180	210	240	270	230	200	cool	cool

To characterize the microstructure of the solder joint, the specimens were mounted, cross-sectioned, polished for optical microscope investigation. They were etched (5% HNO_3 +95%methanol) and observed by a JOEL JSM-5410LV Scanning Electron Microscopy (SEM) under an accelerated voltage 20kV. At the same time, Energy dispersed X-ray (EDX) was used to identify the material elements present in each selected area in the solder joint. The phases formed at the interface were identified by the X-Ray Diffraction (XRD) analysis on the plan view by etching away the Sn matrix. The XRD analysis was conducted on a Philips X-pert Powder Diffractometer employing Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, $DS=0.25^\circ$). The X-ray tube was operated at 40 kV and 40 mA. The X-ray diffractograms were recorded at a step size of 0.02° in the range $10^\circ \leq 2\theta \leq 120^\circ$ with 5 s count accumulation per step. Digital imaging techniques were employed in the measurement of the average IMC growth thickness. Two

polylines R1, R2 were created manually along the edge of the IMC by using the tracing tool. Then the average distance between the two polylines will be given automatically. The thickness results were defined by spatial calibration. The minimum and maximum distance between the two lines will also be marked in the image.

3.2 MICROSTRUCTURE OF SAC SOLDER JOINT

A representative cross-sectioned microstructure of the SAC BGA solder joint is shown in Figure 3-1.

Figure 3-1 Microstructure of as-reflowed Single BGA SAC387 solder joint (I) Sn-rich surrounded by small intermetallic, (II) a large Ag₃Sn rod formed in solder matrix and (III) the interfacial structure

It consists of a single BGA 95.5Sn-3.8Ag-0.7Cu solder ball, soldered between two FR4 substrate parts with copper pads. The ENIG (or Ni/Au) surface finish on copper pad has a nickel (Ni) layer thickness of 5 microns and a gold (Au) flash thickness of 0.05 micron. The copper pad thickness is 30 microns. The FR4 substrate has dimensions of 12mm x 3mm x 0.5mm. The solder reflow profile with a peak temperature of 250 °C and time above melting point of 120 seconds was used. The microstructure of the solder joint after reflow typically consist of globular Sn rich phases surrounded by small Ag₃Sn phases, and Cu₆Sn₅ phases. Some large Ag₃Sn IMC

rods are formed in the solder and the size can be as long as 100 microns or more. The region of interest will be discussed further as (I) Sn-rich surrounded by small intermetallic, (II) a large Ag_3Sn rod formed in the solder matrix, and (III) the interfacial IMC structure in the following sub-sections.

The cross-sectioned microstructure of solder joint specimen on copper pad and ENIG surface finish is shown in Figure 3-2.

Figure 3-2 Microstructure of as-reflowed Solder droplet specimen (a) solder/Cu (b) solder/NiAu/Cu

Lead-free SAC solder paste 95.5Sn-3.8Ag-0.7Cu with a diameter of 5 mm and 0.5mm thickness was placed on FR4 substrate materials on top of a 30 micron thick copper layer. The copper surface finish is with or without the ENIG (Ni/Au) surface finish. The specimens were reflowed using the 8-zone reflow oven. Figure 3-2(a) shows the 95.5Sn-3.8Ag-0.7Cu lead-free solder reflowed directly on Cu pad, and (b) for the Ni/Au surface finish plated on copper pad. The regions of interest for SAC solder on copper pad is indicated in Figure 3-2(a), (I) large hollow-centered Cu_6Sn_5 cube formed in solder matrix, (II) Ag_3Sn rod formed at the interface, (III) interfacial Cu_6Sn_5 intermetallic, and (IV) Sn-rich surrounded by small IMCs, and in Figure 3-2(b), (I) the Sn-rich dendrite, (II) the small intermetallic around the Sn-rich, (III) interfacial NiCuSn IMC. The detailed microstructures will be discussed in the following sub-sections.

3.3 SILVER-TIN IMC IN SOLDER MATRIX

In the SAC solder, large Ag_3Sn structures are often seen in the reflowed solder joints, either in the solder matrix or near interface. The morphology, compositions and solder joint reliability concern are discussed in this section.

3.3.1 Microstructure of Silver-tin IMC

Ag_3Sn is the typical intermetallic presents in SnAgCu solder, most of them are very small needles or rods soaked in the Sn-rich phase as dendrites, as shown in Figure 3-3, which is the high magnification SEM image of the location (I) in Figure 3-1. The typical size of the small needles is about 5 microns. The EDX analysis performed on the needle showed by the arrow in the Figure 3-3(a) confirmed that it is silver-tin IMC. It should be noted that the EDX spectrum can not identify the exact composition of the Ag_3Sn , since the EDX peaks cannot be used quantitatively. The conclusion is made by comparing with other reported EDX spectrums [14], and the actual composition of the

IMC compound can be derived from phase diagrams and X-ray diffraction and EPMA studies.

Figure 3-3 SEM image and EDX features of the Ag_3Sn IMC in SAC387 solder joint (a) Ag_3Sn IMC (b) EDX spectrum of Ag_3Sn

Figure 3-4 Sn-Ag binary phase diagram, the arrow shows the projection of SAC387 alloy on binary phase diagram [96]

In the Sn-Ag binary phase diagram shown in Figure 3-4, it can be seen that when the high concentrated Sn(Ag) liquid phase cools down to the L-S line, the solid phase formed can only be Sn-rich and Ag_3Sn . This means that if EDX analysis proved that

Ag is highly concentrated in a solid phase, it must be Ag_3Sn . Similarly, some other phases were determined in this way. There are other direct methods, such as EPMA (Electron Probe Micro Analyzer), to determine the exact compositions.

Figure 3-5 Large Ag_3Sn IMC plate and EDX features in the SAC solder joint, the SEM image is plot II in Figure 3-1 (a) Sn-rich; (b) Cu_6Sn_5 ; (c) Ag_3Sn

However, not all the Ag_3Sn IMCs are small and distributed uniformly. As reported by T.Y. Lee's [97], the Ag_3Sn are large plates by deep etching away the solder. The SEM image in Figure 3-5 shows the details of location (II) in Figure 3-1. A large plate-like Ag_3Sn structure is studied further. EDX analysis was performed on several locations and the results were shown in Figure 3-5(a-c). Some smaller crystals of Cu_6Sn_5 were found near the sides of the Ag_3Sn plate. And the dark background was the Sn-rich phase. The Sn rich phase forms first upon solidification due to lower nucleation barrier compared to IMCs. The Ag and Cu in the remaining liquid phase reaches an

extent for the IMC phases to nucleate and a pseudo-eutectic structure forms in the interdendritic spaces. Since Ag has a higher concentration compared to Cu, Ag_3Sn can nucleate and grow rapidly in larger volume, and the large plate are shown in Figure 3-5. Kang et al [98, 99] reported that the growth of large Ag_3Sn is critically affected by the cooling rate during reflow. With a high cooling rate, such as $1.5^\circ\text{C}/\text{sec}$ or higher, the formation of large Ag_3Sn can be kinetically suppressed. However, for the typical reflow profile used in this study, the cooling rate near 217°C is lower than $0.5^\circ\text{C}/\text{sec}$. Thus, the solder reflow process generates non-uniform growth of eutectic structures.

The large Ag_3Sn can form either in the solder matrix or near the Solder/UBM interface. Figure 3-6 (a-f) showed six large Ag_3Sn formed in the solder, in which (a) and (b) were located in the solder matrix. (c) and (d) were located on the Solder/Ni(Au) interface. (e) and (f) were located on the Solder/Cu interface.

Figure 3-6 Large Ag_3Sn formed at different locations in the solder joint (a) and (b) are located in the solder matrix. (c) and (d) are located on the Solder/Ni(Au) interface. (e) and (f) are located on the Solder/Cu interface

Study of the Ag_3Sn features observed in 50 specimens show a total of 173 Ag_3Sn IMCs (longer than 50 microns), 64% are connected to the Cu or Ni interface, and 36% are dispersed in the solder matrix. This shows that the solder joint interface is prone to the Ag_3Sn large plates formation. Ag_3Sn intermetallic nucleates more readily at the interface, where the interface IMC act as nucleation seeds for Ag_3Sn formation.

3.3.2 Silver-tin Plates Reliability Concerns

The large Ag_3Sn plates can cause reliability problems when it forms at a high stress concentration area, such as the interface and corner between solder bump and copper pad. Fatigue cracks can initiate and propagate along the interface between the Ag_3Sn and solder, leading to mechanical failure.

Figure 3-7 shows the effect of the presence of Ag_3Sn at the interface. A constant shear stress 4MPa was applied on the lap-shear solder joint specimen under the isothermal aging temperature of 125°C. Two Ag_3Sn plate were found on this polished specimen by optical microscopy. The microscope was placed outside the chamber. After each 24 hours interval, the thermal chamber was opened and surface

morphologies were recorded. The direction of the shear stress is indicated by the arrow in Figure 3-7.

Figure 3-7 Deformation of Ag_3Sn under thermal-mechanical aging at 125 °C, Ag_3Sn rotates subject to the stress, crack forms near the IMC plate

Under the imposed stress at 125 °C, rotation of the Ag_3Sn IMC by about 20° for the both Ag_3Sn was observed during isothermal-mechanical aging. For example, the

Ag₃Sn on the left shows that one end of the Ag₃Sn plate was fixed to the interface. While the other end of the Ag₃Sn plate moved by 17 microns to the right. During this process, the cracks initialed and extend along the interface of the Ag₃Sn and solder, shown as the arrows in the Figure 3-7.

Since the Sn-rich phase is a viscoplastic material and is very soft at 125 °C, it is actually creeping under the shear stress. However, the presence of the Ag₃Sn plates is a barrier for the movement of Sn-rich phase since Ag₃Sn is much harder than the Sn-rich matrix. Thus a high stress area exists near the Ag₃Sn IMC and cracks initiate and propagate in the area near Ag₃Sn.

3.4 COPPER-TIN INTERMETALLIC IN SOLDER MATRIX

It is assumed that the microstructure of the SnAgCu solder matrix after reflow are Sn rich phases surrounded by Ag₃Sn intermetallic precipitates with some Cu₆Sn₅ precipitates. In this study, the microstructure of the eutectic area was carefully examined under high magnification SEM and EDX analysis. The results showed that not all precipitates are Ag₃Sn, as some areas were found to be Cu₆Sn₅ dominant structure. A typical Cu-Sn IMC area is shown in Figure 3-8, where the intermetallic was mainly features are line dot-like particles. EDX analysis confirmed that these dots were mainly Cu-Sn IMC.

Some large hexagonal hollow-centered Cu₆Sn₅ IMC rods were observed in the 95.5Sn-3.8Ag-0.7Cu solder matrix. But the Cu₆Sn₅ rods are mainly seen in 95.5Sn-3.8Ag-0.7Cu/Cu system, as shown in Figure 3-9 (a-e), especially for the specimen with longer reflow time. Figure 3-9(a) and (b) show the solder droplet specimen microstructure where the reflow profile that the soak temperature above 217 °C is 600 seconds. It can be seen that not only the interfacial IMC grew to a high thickness. Some

hollow-centered hexagonal Cu_6Sn_5 structures were developed near the interface, as highlighted by the arrows.

Figure 3-8 SEM image and EDX features of the Cu-Sn IMC

But for 95.5Sn-3.8Ag-0.7Cu/Ni(Au) system, this type of large Cu_6Sn_5 is rarely seen, and exist as shown in Figure 3-9(f), in sizes much smaller compared to that for Solder/Cu system. This suggests that the Cu-Sn IMC was contributed by the copper pad. During the reflow process, copper dissolved into the solder matrix from the copper pad. NiAu surface finish can effectively stop the diffusion of Cu from copper pad and act as an effective barrier layer preventing the formation of large Cu_6Sn_5 .

The hexagonal hollowed-centered Cu-Sn IMC structure (actually it is filled with Sn-rich, which is etched away before observation) was reported by Frear et al. [100] also for SnPb solder. He suggested that large Cu_6Sn_5 form in the solder matrix by a screw dislocation mechanism and that hollow-type Cu_6Sn_5 result when the core of the rod dissolves away because of its higher energy, and is filled with molten solder. When the long Cu_6Sn_5 whiskers break off into the low-Cu matrix, redissolution begins at the core of the rod, which is replaced by molten solder. Unlike Ag_3Sn plate, the Cu_6Sn_5 rod does not have too much mechanical effect on the solder properties due to its lower volume and smaller size.

Figure 3-9 Hollow-centered Cu_6Sn_5 intermetallic rods in solder matrix after etching

3.5 INTERFACIAL MICROSTRUCTURES AND COMPOSITIONS

The interfacial IMC microstructures of the 95.5Sn-3.8Ag-0.7Cu/Cu system and 95.5Sn-3.8Ag-0.7Cu/Ni(Au)/Cu system were observed by SEM. The different morphologies were compared. The composition of intermetallic formed at the 95.5Sn-3.8Ag-0.7Cu/Ni(Au)/Cu interface was examined by EDX and XRD.

3.5.1 Morphologies of the Interface IMC

The typical interfacial morphologies for Solder/Cu system and Solder/ENIG/Cu system are shown in Figure 3-10(a) and (b), respectively. The scallop-like intermetallic formed on the solder/Cu interface for Cu_6Sn_5 as shown in Figure 3-10(a). For Solder/ENIG/Cu system, it can be seen that after reflow, the IMC on the solder/nickel interface are irregular and needle like in feature.

Figure 3-10 Interfacial morphologies on different surface (a) Cu, (b) ENIG

The compositions of the IMC needles on Solder/ENIG/Cu interface could not be determined by earlier reports. Shiau et. al. [14] reported that its composition and microstructure is very sensitive to different solder and operation process. It can be $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ ternary intermetallic, $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$ ternary intermetallic, and even Au substituted quaternary intermetallic. The ENIG surface finished is widely used in soldering devices, the intermetallic compositions for 95.5Sn-3.8Ag-0.7Cu/ ENIG/Cu interface was further examined.

3.5.2 Characterization of the Intermetallic Compositions

The SEM image in Figure 3-11 shows the morphology of solder/nickel interface of the single BGA solder joint. This is the enlarged image of location (III) shown earlier in Figure 3-1.

Figure 3-11 IMC and EDX features at the Solder/ ENIG interface, plot III in Figure 3-1
 (a)Ag₃Sn IMC;(b) Sn-rich; (c)(Ni_{1-x}Cu_x)₃Sn₄ IMC; (d)Ni metallization layer; (e)Cu pad

EDX analysis was used to identify the traces of respective elements noted at the IMC layer. The darker phase above the IMC is the Sn rich matrix. The lighter features are Ag₃Sn and Cu₆Sn₅ precipitates. The Ni metallization layer is approximately 5μm thick, and contains about 6wt% phosphorus resulting from Ni-plating procedure.

The darker phase below the Ni layer is the copper pad. IMC formed between solder and Ni/Au surface finish on copper pad is quite sensitive to the reflow profile

and materials used. Based on the EDX analysis in Figure 3-11(c), it is not clear what the exact phase and chemical composition of the IMC is. Although the element Sn, Ni and Cu were identified, as the thickness of the IMC is about 1 micron in feature size and this is close to the minimal EDX spot size. Thus the background Sn-matrix may also be deflected, giving stronger Sn element peaks in the EDX spectrum.

In order to determine the composition and morphology of IMC on the interface, the solder droplet specimen was used to examine the IMC layer from planar view after selectively etching away the Sn matrix using 13vol % nitric acid in DI water. XRD and SEM analysis were employed for phases and morphology studies. The plan view of the IMC is shown in Figure 3-12. There are many needle-like IMCs located on the plan view. Their typical sizes range from 5-10 μm in length and 1-2 μm in width. Figure 3-13 shows the XRD pattern of the plan view specimen. The major phase turned out to be Ni_3Sn_4 by matching search with the data from International Centre for Diffraction Data (ICDD), and peaks of Ni substrate were also detected, the intensity is much lower compared to Ni_3Sn_4 . Combined with the EDX result that Cu is present in the needle-like IMC, it is Cu substituted $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$.

Figure 3-12 Plan view of Solder/Nickel interface after etching away the Sn matrix

Figure 3-13 XRD pattern of Solder/ENIG interface (□)Ni₃Sn₄; (■)Sn; (●)Ni

Figure 3-14 Ni-Cu-Sn ternary phase diagram, top view. The marked area is the possible composition to form $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$, x can range from 0 to 0.10

From Chen's study [101] of the Sn-Cu-Ni ternary system and a Sn-Cu-Ni ternary phase diagram shown in Figure 3-14, it can be seen that x , the portion of Cu here can range from 0 to 0.10 while keep the Ni_3Sn_4 crystal structure unchanged. Considering the different local situation for each needle, these needles do not have to have the same

percentage of Cu. Further studies can be conducted to obtain the Cu percentage in the IMC, by using Electron Probe Micro Analysis (EMPA) to quantitatively measure the composition of the NiCuSn IMC needle.

3.5.3 Effect of Soldering Time on IMC Growth

The reflow profile can affect the quality of the solder joint, especially the intermetallics formed at the solder joint interface. The peak temperature and reflow time are the major factors. The temperature profile in the 8-zone reflow oven can be programmed at different reflow conditions for the 95.5Sn-3.8Ag-0.7Cu solder. In this study, the effect of reflow time on the interfacial IMC was examined by changing the rolling belt speed. As for this temperature profile, when the belt speed was set as 50 cm/min, the reflow time above the melting point 217 °C was 120 seconds. The reflow peak temperature was 250 °C. Different belt speeds 10, 30, 50, 70, 90, 110 cm/min were used for comparison, the reflow time above 217 °C were 600, 200, 120, 86 second, 67 and 54 seconds, respectively. The cross-section of the solder droplet specimens with different reflow time was observed by the SEM. The images for solder/Cu system were shown in Figure 3-15(a-f).

It can be seen that, with the increase of the reflow time, the size of scallop-like Cu_6Sn_5 interfacial intermetallic increased rapidly. For the specimen with 54 sec reflow time, shown in Figure 3-15(a), the average intermetallic thickness was only 0.9 microns, while for the specimen with 600 seconds reflow time, shown in Figure 3-15(f), the intermetallic thickness increased to 9.1 microns. Even for the specimens with the longest reflow time, the shape of the Cu_6Sn_5 maintains its scallop-like feature. It grows from the copper pad and extend to the solder matrix.

Figure 3-15 Cross sectional SEM images at the interface, solder/Cu with different reflow time (a)54 sec (b)67 sec (c)86 sec (d)120 sec (e)200 sec (f) 600 sec

The images for solder/ ENIG/Cu system are shown in Figure 3-16(a-d). With the increase of the reflow time, the thickness of the $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ interfacial intermetallic did not increase very much. For the specimen (a) with 54 sec reflow time, the average intermetallic thickness was only 0.6 microns, while for the specimen (d) with 600 seconds reflow time, the intermetallic thickness increased to 3.1 microns. Compared to solder/Cu system, the growth rate for nickel-tin intermetallic is much lower due to the lower solubility of Ni in Sn liquid between 217 to 250 °C. This is expected as Ni acts as

the barrier layer to protect the copper pad. The morphology of the Ni-Sn intermetallic also changes dramatically upon the reflow time, as shown in Figure 3-16.

Figure 3-16 SEM image of Interfacial morphology solder/ ENIG/Cu with different reflow time (a)54 sec (b)120 sec (c)200 sec (d)600 sec

The formation of the interfacial intermetallics during soldering is a liquid/solid reaction, where the liquid is the melted lead-free solder (95.5Sn-3.8Ag-0.7Cu), and the solid is the copper pad or ENIG surface finish. The intermetallic nucleated and grew between the liquid/solid couple and a layer of intermetallic will develop on the top of the original solid surface. Gagliano et al [102] examined the pure liquid tin/solid copper system at high isothermal temperatures from 250°C to 325 °C, and quantitatively evaluated the thickness of the Cu_6Sn_5 intermetallic, and modeled the growth behavior using time and temperature dependant empirical power-law equations.

In this study, the intermetallic thickness was measured by the digital imaging method [103], and the result was plotted against reflow time above melting point at 217

°C, and shown in Figure 3-17. By comparing the Cu_6Sn_5 thickness obtained in our study with Gagliano's data, it is interesting to see that, although the trends of the thickness-time plot were similar, the thickness obtained in our study is much higher. For example, in Gagliano's report, the thickness of Cu_6Sn_5 after 600 second reflow time at 250 °C is only 3.92 microns, while in our study, it is 9.1 microns. The pure Tin/copper system reported by Gagliano may have more Cu dissolved into the solder matrix, and less remain at the interface to form interfacial intermetallic. In our study, the 95.5Sn-3.8Ag-0.7Cu/Cu system affects copper diffusion from the solder to form faster interfacial IMC growth.

Figure 3-17 Intermetallic thickness subject to reflow time

The results shown in Figure 3-17 will help engineers to select suitable required to optimize the IMC volume and thickness. Further studies on intermetallic growth subject to solid state thermal aging will be covered in chapter 4.

3.6 SUMMARY

The two major IMCs in solder matrix, Ag_3Sn and Cu_6Sn_5 , and interface IMC were investigated. The Ag_3Sn and Cu_6Sn_5 exist as dispersed precipitates as needle or

rods. The size is several microns. Some large scale plate-like Ag_3Sn and hexagonal hollow-centered Cu_6Sn_5 rods IMC also form during the reflow process. The interface IMC formed in 95.5Sn-3.8Ag-0.7Cu/Cu and 95.5Sn-3.8Ag-0.7Cu/ENIG/Cu solder joint were characterized and their different composition, morphology and IMC growth behavior were reported. The compositions of the IMC on the Ni surface finish were examined by EDX and XRD. The needle like intermetallic formed on the interface in this study was confirmed to be Cu substituted $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$. The effect of the reflow time on the interfacial intermetallic was examined on both solder/Cu and Solder/ENIG/Cu system. For solder/Cu system, the morphology of the Cu_6Sn_5 is scallop-like in feature. With different reflow time, the size of Cu_6Sn_5 interfacial intermetallic increases rapidly. The growth rate of nickel-tin intermetallic is much lower, but the morphology changes dramatically with the reflow time.

CHAPTER 4 THERMAL AGING EFFECT ON IMC GROWTH

The growth of interface intermetallic compounds (IMC) between SAC solder with Cu-pad and ENIG surface finish is a long-term solder joint reliability concern. The growth rate of the IMC layer can affect the solder joint performance subject to reliability test. In this section, IMC growth mechanism subject to isothermal and thermal cycling aging is demonstrated.

4.1 BACKGROUND

Electronic assemblies are soldered on to the printed wiring board by reflow process, with peak reflow temperatures 20°C-30°C above the liquidus temperature of the solder alloy. Metallurgical reaction between liquid solder and copper pad or pad with ENIG metallization forms intermetallic compound (IMC) layer or layers at the solder/metallization interface. The thickness of this IMC layer is a major concern because the embrittlement of the solder joint interfaces can cause solder joint reliability problems. A thin layer of IMC promotes good wetting and results in a good metallurgical bond. A thick IMC layer can result in weaker solder joint interface strength. Drinfeld and Ramon [104] reported that the shear strength of the solder joint is the maximum when the IMC layer thickness is about 1.2 μm . Liu et al [105] also showed that the shear and tensile strengths of the flip-chip solder joints decrease with increasing reflow time and IMC thickness. A long aging time will result in excessive consumption of metallization layer or copper pad thickness and weaken the solder joint interface. Therefore, it is important to understand the growth behavior of IMC layers in the soldering process and during solid state reaction resulting from thermal aging.

In accelerated thermal cycling (ATC) tests, cyclic temperatures (between -40°C to

+125°C) causes concurrent degradation of the solder joint resulting in IMC growth and thermal fatigue damage[106,107]. The study of IMC growth behavior for isothermal annealing and thermal cycling aging is important as it affects the long-term solder joint reliability performance of soldered assemblies.

In this study, thermal aging effect on IMC growth between solder and substrate were investigated for isothermal and thermal cycling aging conditions. The growth kinetics of the Ni-Cu-Sn IMC layer between Sn-3.8Ag-0.7Cu (SAC387) and ENIG (Ni/Au) surface finish subject to corresponding isothermal aging at 125°C, thermal shock (-55 °C to +125 °C) and thermal cycling (-40 °C to +125 °C) profiles were investigated. A methodology for predicting the IMC layer growth behavior for long-term thermal cycling profiles was developed. Measured results of interfacial IMC growth between SAC387 solders and ENIG surface finish on copper pad are reported. Thermal cycling fatigue failure was investigated and correlated with IMC growth for lead-free PBGA assembly.

4.2 EXPERIMENTAL PROCEDURES

The droplet specimen and single BGA solder joint specimen were used to study the growth of IMC during the isothermal and thermal cycling aging. Isothermal aging at 125 °C, Thermal Cycling (TC) and Thermal Shock (TS) were used for solid state IMC growth studies. Isothermal aging at 125°C were carried out in a thermal chamber from 50 to 300 hours. The TC profile is -40°C to +125°C with a cycle time of 56 minutes, a ramp rate of 12.7 °C/min and a hold time of 15 minutes. The TS profile is -55 °C to +125°C with a cycle time of 17 minutes, a ramp rate of 51.4 °C/min and hold time of 5 minutes. The solder joints were subjected to TC and TS aging for 500, 1000 and 2000 cycles. The exposure time is equal to the total dwell time spent at the high temperature

soak period for the TC and TS profile respectively. After thermal aging, the lap shear specimens were mounted, cross-sectioned, polished for optical microscope investigation. Then they were etched (5% HNO_3 +95%methanol) and observed by a JOEL JSM-5410LV Scanning Electron Microscopy (SEM) under an accelerated voltage of 20kV. Digital imaging techniques were employed in the measurement of the average IMC growth thickness. Two polylines R1, R2 were created manually along the edge of the IMC by using the tracing tool. Then the average distance between the two polylines were calculated automatically. The minimum and maximum distance between the two lines will also be marked in the image.

Thermal cycling test and fatigue failure characterization were conducted on PBGA sample. The PBGA specimen consists of 316 I/O PBGA with SAC387 solder balls. The ENIG (Ni/Au) surface finish on copper pad has a nickel (Ni) layer thickness of 5 microns and a gold (Au) flash thickness of 0.05 micron. The copper pad thickness is 30 microns. The packaging substrate material is bismaleimide-triazine (BT), board materials is fire retardant polymer/glass fiber cloth laminate (FR-4), flux used in solder reflow is synthetic activated flux (SA). The PBGA assembly is shown as in Figure 4-1.

Figure 4-1 SAC387 PBGA 316 I/O component and the cross-sectioned solder joint

The distribution of SAC387 solder joints in $35 \times 35 \text{ mm}^2$ 316 I/O PBGA is shown in

Figure 4-2. There are five perimeter rows with 300 solder balls and 16 solder balls at the center giving a total of 316 solder joints. The numbering method is shown in Figure 4-2.

Figure 4-2 Numbering of solder balls for 316 I/O PBGA component. (TC failure often occurs at the component or dies corner as circled in the Figure)

The in-situ micro-deformation in the PBGA solder joints subject to thermal loading were measure by the Micro-DISC system. The system is based on the principle of digital image speckle analysis (DISA) measurement. The PBGA assembly was sectioned and polished along the symmetric plane for DISA measurement. The solder joints located at the reliability concerned positions, for example at the outmost solder joint at the corner of the whole BGA (A1,A20, T1, T20), the corner joints located underneath the corner of the silicon die (I9, I12, L9, L12) and some other solder joint were chosen for analysis (See appendix II for more information about DISA).

The cross-sectioned solder joint row A and row I is shown in Figure 4-3. Measurements were taken at room temperature of 25°C and elevated temperature of 75°C, 125°C. A pair of digital images acquired at the un-deformed state at room temperature and the deformed state at elevated temperature was correlated using the DISA technique. The deformation and strain fields were calculated.

Figure 4-3 PBGA assembly and sectioned interface

The PBGA specimens were subjected to TC aging for up to 3000 cycles (five samples). Then they were cross-sectioned and observed by SEM. The outmost 20 solder joints were investigated first then they were grinded away to the second column for further investigation.

4.3 IMC MORPHOLOGY CHANGES

The solder reaction continues with time during the thermal aging process. This is evidenced by the morphology change and growth in thickness of the IMC layers when compared to the as-reflowed IMC thickness.

4.3.1 IMC between SAC solder and ENIG Finish

Single BGA specimens with a reflow time of 120 seconds were used for aging studies. Typical cross-sectional interfacial microstructures of the SAC Solder/ENIG system after aging are shown in Figure 4-4 for 0, 119 and 262 hours of isothermal aging at 125°C.

The NiCuSn ternary IMC on the solder/nickel interface after reflow are irregular and grow in needle-like manner, as show in Figure 4-4(a). After 119 hours of aging, coalescence of the IMC needles leads to lateral thickening and ripening. The needle-like IMC do not grow in length as they coalesce laterally, as shown in Figure 4-4(b).

After 262 hours of aging, the needles have transformed to an IMC layer growth as shown in Figure 4-4(c).

Figure 4-4 SEM images of IMC morphology change subject to isothermal aging (a) 0h; (b) 119h; (c) 262h

4.3.2 IMC Between SAC solder and Cu Pad

The interfacial intermetallic between SAC and Cu pad before and after isothermal aging at 125°C is shown in Figure 4-5. The copper–tin intermetallics formed when molten solder reacted with the copper substrate surface, as shown in Fig 4-5(a). The morphology and thickness of Cu-Sn IMC for the as-reflowed specimen are dependent on the reflow time, cooling rate and the solder materials itself. Typically the IMC is scallop-shaped and extend to Sn matrix. From Sn-Cu phase diagram, it can be seen that intermetallic phase is a double layer with Cu_3Sn on the copper substrate and Cu_6Sn_5 in contact with the molten solder. For as-reflowed specimen, there is only one IMC layer, Cu_6Sn_5 , could be seen after reflow process. After 120 hrs of aging, Cu_3Sn layer started to grow and become visible, as shown in Fig. 4-5(b). Subsequently, the thickness of

the intermetallic layers increased with the number of thermal cycles. The intermetallic layers for the solder joints exposed to 240 hrs are shown in Fig.4-5(c).

Figure 4-5 SEM (BSE mode) image of SAC Solder to Copper pad interface before and after isothermal aging, (a) as-reflowed (b) after 120 hrs (c) after 240 hrs, the IMC layers were Cu_6Sn_5 and Cu_3Sn

4.4 ISOTHERMAL IMC GROWTH KINETICS

During the soldering process, when the molten solder comes into contact with the substrate, it leads to the formation of IMC layer at the solder/substrate interface. This IMC layer grows in thickness during the soldering process itself and during solid-state thermal aging condition. In this section, intermetallic growth kinetics was analyzed based on the isothermal aging result. Several parameters determined in this section will

be used in the subsequent discussion for non-isothermal aging such as thermal cycling (TC) and thermal shock tests.

4.4.1 Measurement of IMC Thickness

IMC thickness was measured on back-scattered SEM (BSE) images. Some of the IMC measurement measurements were processed from the optical microscope images without etching. By using optical microscope, the needle-like $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ IMC on the solder/nickel can be readily observed on a cross-sectioned surface without etching. For secondary electron SEM (SE), etching process must be used first before observing the IMC details. A problem is that those IMCs behind the surface can also be seen as shown in Figure 4-4. When using the digital imaging technique with such SEM image, higher average IMC layer thickness will be computed. Thus, optical images (see Figure 4-6) or BSE images (see Figure 4-5) are more suitable for determining the IMC layer thickness without interface etching. The namely “thickness” for the as-reflowed solder joint is calculated from taking the area under the peak curve divided by the length of the interface used for digital processing.

Figure 4-6 IMC thickness measurement during isothermal aging 125 °C (optical image)

(a) 47h ;(b)119h; (c)167h; (d)262h;

The measured results for isothermal aging at different temperature, 150 °C, 125 °C and 100 °C are given in Table 4-1. It can be seen that at 150°C, the IMC growth is very fast, after 290 hrs isothermal aging (~12 days), the thickness reached 6.767 µm; For 125°C, after 262 hours, it is 2.7 µm, and for 100 °C after 290 hours, it is only 1.7 µm. Isothermal aging was also performed at 75 °C, but there was no observable morphology change and IMC growth during the time tested of 290 hrs and shows that isothermal aging below 100 °C will take a long time to develop IMC thickness data.

Table 4-1 IMC thickness upon isothermal aging time at different temperature

150 °C		125 °C		100 °C	
Time (*3600s)	Thickness (10 ⁻⁶ m)	Time (*3600s)	Thickness (10 ⁻⁶ m)	Time (*3600s)	Thickness (10 ⁻⁶ m)
0	1.35	0	1.35	0	1.35
48	3.517	47	1.897	48	1.493
120	4.72	119	2.113	120	1.542
170	5.614	167	2.403	170	1.615
290	6.767	262	2.695	290	1.689

The thickness data were plotted subject to isothermal aging time, as shown in Figure 4-7. The IMC thickness growth rate decrease gradually with the aging time. The exact growth model will be analyzed in the next sub-section.

Figure 4-7 IMC thickness growth subject to isothermal aging time

4.4.2 Isothermal IMC Growth Model

The growth kinetic parameters of the IMC layer were determined by plotting the measured IMC layer thickness against the exposure time, at isothermal temperatures tested [103]. The IMC data were fitted using a power law equation as shown in empirical Eqn 4-1.

$$x = x_0 + At^n \quad (4-1)$$

where x is the IMC layer thickness at time t , x_0 is the IMC layer thickness in the as-soldered condition, A is a constant and n is the time exponent. The temperature dependence of the growth constant A is given by the Arrhenius type equation as shown in Eqn 4-2.

$$A = A_0 \exp\left(-\frac{\Delta H}{RT}\right) \quad (4-2)$$

where, A_0 is pre-exponential factor, ΔH is the apparent activation energy for the growth, R is the gas constant (8.314 J/K•mol) and T is the absolute temperature. Thermal annealing test was conducted at various temperatures. A_0 and ΔH can be determined. Combining Eqn 4-1 and Eqn 4-2, IMC thickness becomes a function of two variables, time and temperature,

$$x = x_0 + A_0 t^n \exp\left(\frac{-\Delta H}{RT}\right) \quad (4-3)$$

However, it must be noted that Eqn 4-3 is for isothermal aging condition where temperature is constant over time. For thermal cycling aging, temperature varies as a function of time. Thus the growth constant, A , become time-dependant and the IMC thickness is the accumulation of the IMC thickness of different temperatures over accumulated time. The IMC layer growth rate, v , is temperature and time dependant. The IMC thickness after thermal cycling aging can be determined by integrating the IMC growth rate over time. The following sub-sections, will deal with the IMC growth kinetic mechanism for isothermal annealing compared to thermal cycling aging. Models to analyze the IMC growth subject to thermal cycling aging are proposed.

4.4.3 Determination of Coefficients in Growth Model

The NiCuSn IMC growth model for isothermal aging is determined in this section. The constants in Eqn 4-3 are obtained by curve fitting the experimental IMC data measured in Table 4-1. Take logarithm of Eqn 4-3,

$$\ln(x - x_0) = \ln(A) + n \ln(t) - \Delta H / RT \quad (4-4)$$

A multivariable linear regression analysis was performed on the data obtained in Table 4-1 according to Eqn 4-2. The independent variables were $\ln(t)$ and $1/T$; the

dependent variable was $\ln(x-x_0)$. The regression analysis returned the coefficient $\ln(A)$, n and $\Delta H/R$, from which the respective kinetics parameters, A , n and ΔH were determined.

The result for $\ln(x-x_0)$ versus $\ln(t)$ is shown in Figure 4-8. The unit of IMC thickness and time were meter and second, respectively. The three curves are for IMC data at in 150°C, 125°C, 100°C and the results are given in Eqn 4-5; from which the time exponent, n , was determined as 0.51 ± 0.02 . The values of the square of the correlation coefficient, R_c^2 , were 0.997, 0.963 and 0.961 respectively. This show that the growth of NiCuSn IMC is a diffusion-based mechanism.

Figure 4-8 Analysis of $\ln(x-x_0)$ versus $\ln(t)$ to determine the time exponent

$$T=150\text{ }^{\circ}\text{C}, \ln(x-x_0) = 0.5157 \ln(t) - 19.265 \quad R_c^2 = 0.9965$$

$$T=125\text{ }^{\circ}\text{C}, \ln(x-x_0) = 0.5268 \ln(t) - 20.805 \quad R_c^2 = 0.9628$$

$$T=100\text{ }^{\circ}\text{C}, \ln(x-x_0) = 0.4881 \ln(t) - 21.689 \quad R_c^2 = 0.9613 \quad (4-5)$$

The result for linear analysis of $\ln(x-x_0)$ versus $1/T$ was shown in Figure 4-9. The trend line for the four curves after 48h, 120h, 170h and 290h are give in Eqn 4-6. The apparent activation energy, ΔH , was determined as 72.9 ± 2.1 kJ/mol. By combining the result of time exponent and ΔH , the coefficient A can be determined as $A = 4.92 \pm 0.32$.

$$\begin{aligned}
 48h, \quad \ln(x-x_0) &= -8564.1(1/T) + 7.1675 & R_c^2 &= 0.9981 \\
 120h, \quad \ln(x-x_0) &= -9022.4(1/T) + 8.6785 & R_c^2 &= 0.9967 \\
 170h, \quad \ln(x-x_0) &= -8754.2(1/T) + 8.2959 & R_c^2 &= 0.9984 \\
 290h, \quad \ln(x-x_0) &= -8732.6(1/T) + 8.485 & R_c^2 &= 0.9985 \quad (4-6)
 \end{aligned}$$

Figure 4-9 Plot of $\ln(x-x_0)$ vs $1/T$ for activation energy study

$$T=150\text{ }^{\circ}\text{C}, \ln(x-x_0) = 0.5157 \ln(t) - 19.265 = 0.5157 \ln(t) + \ln(A) - \Delta H/RT$$

$$T=125\text{ }^{\circ}\text{C}, \ln(x-x_0) = 0.5268 \ln(t) - 20.805 = 0.5268 \ln(t) + \ln(A) - \Delta H/RT$$

$$T=100\text{ }^{\circ}\text{C}, \ln(x-x_0) = 0.4881 \ln(t) - 21.689 = 0.4881 \ln(t) + \ln(A) - \Delta H/RT \quad (4-7)$$

Finally, the Ni-Sn IMC thickness $x(m)$ as a function of solid-state aging isothermal time $t(s)$, and temperature $T(K)$ is predicted by,

$$x = (1.35 \pm 0.2) \times 10^{-6} + 4.92t^{0.51 \pm 0.02} \exp[-(72.9 \pm 2.1) \times 10^3 / RT] \quad (4-8a)$$

$$x = (1.35 \pm 0.2) \times 10^{-6} + 4.95t^{0.5} \exp[-(72.6) \times 10^3 / RT] \quad (4-8b)$$

After numerical analysis, n was determined as 0.51. This indicates that the IMC growth is diffusion controlled mechanism (see Eqn 4-8a). Hence by choosing n as 0.5, the equation can be curve-fitted again by adjusting other parameters. The constant A_0 and ΔH would be 4.95 and 72.6 (kJ/mol), respectively (See Eqn. 4-8b). Growth kinetics for various IMC layers between various solder/substrate couples was reported in the literatures [108-112]. Table 4-2 lists a summary of reported n and ΔH values in pure Sn/Cu, SAC/Cu and SAC/ENIG diffusion couples. For solder/Cu couples, when both η -phase and ε -phase present, their individual thickness can be measured for different growth temperatures and times and the corresponding n and ΔH values can be determined. The total IMC layer thickness was also analyzed and a “combined” n and ΔH were obtained.

For IMC layer on Sn/Cu interface, investigations by Vianco *et al* [109] showed that the combined apparent activation energy, ΔH , for the growth of total IMC layer ($Cu_6Sn_5 + Cu_3Sn$) in pure Sn/Cu diffusion couples is 66 kJ/mol when temperature ranges from 70°C to 170°C, while it is 41.7 kJ/mol in SAC/Cu couple. This indicates that there is a significant effect of solder alloy composition on the growth of IMC layer, the reason for pure Sn/Cu couple that needs higher activation energy is its higher melting temperature than SAC. The apparent activation energy, ΔH , varies significantly between the authors, too. Such a variation is due to the difference in the resultant microstructure of the IMC layer because of the differences in processing the diffusion couples. The diffusion of Cu and Sn through the IMC layer depends on the grain size

and the morphology of the layer. It can greatly influence the growth rate of the IMC layer. The growth kinetic parameters of IMCs are listed in Table 4-2.

Table 4-2: Time exponent and apparent activation energy for the IMC layer growth on Solder/Cu or ENIG substrate

Reaction couples	Soldering method	T / °C	Time expo. *(n)			ΔH kJ/mol			Ref.
			Cu ₆ Sn ₅	Cu ₃ Sn	total	Cu ₆ Sn ₅	Cu ₃ Sn	totald	
Pure Sn/Cu	Hot dipped	100-170	0.5*	0.5	--	84	57	77	[108]
	Electroplated	170-205	--	0.5	0.5	--	43	25	[109]
	Electroplated	70-170	--	--	0.42	--	--	66	[109]
SAC387/Cu	Reflowed	125			0.5	--	--	--	[52]
	Reflowed	100-150	--	--	0.48	--	--	41.7	Author
SAC387/Ni	Reflowed	100-150	0.51((Ni _{1-y} Cu _y) ₃ Sn ₄)			72.9(Ni _{1-y} Cu _y) ₃ Sn ₄			Author

* Values of n=0.5 are assumed values. That is, the thickness data are plotted against square root of time and fitted with a straight line

4.5 THERMAL CYCLING IMC GROWTH KINETICS

4.5.1 Proposed Thermal Cycling IMC Growth Model

The isothermal IMC growth parameters n , A , ΔH are constants over a range of isothermal temperatures from 100 to 150 °C. Hence, the same IMC growth kinetics may be applied for temperature above 100 °C for thermal cycling aging. The IMC layer growth parameters obtained from isothermal annealing is used in formulating an IMC layer growth model under thermal cycling aging. The mathematical work below is based on IMC thickening process that follows from Eqn 4-3.

For a thermal cycling aging process, IMC growth rate, v , can be defined as a function of x and T ,

$$v = \frac{dx}{dt} = \frac{1}{x^m} A' \exp(-\Delta H' / RT) \quad (4-9)$$

where x is the current layer thickness, T is temperature, m is the thickness exponent. A' and $\Delta H'$ are coefficients to be determined. R is the universal gas constant,

8.314 J/mol·K. Eqn 4-9 can be rearranged to Eqn 4-10 and integrated to give Eqn 4-11,

$$x^m dx = A' \exp(-\Delta H' / RT) dt \quad (4-10)$$

$$\int_{x_0}^{x_t} x^m dx = \int_0^t A' \exp(-\Delta H' / RT) dt \quad (4-11)$$

Since Eqn 4-11 depends on temperature profile, T(t), to determine the coefficients m, A', ΔH', let T=constant, the integral equation is expressed as,

$$x_t = x_0 + \left[(m+1) A' \right]^{\frac{1}{m+1}} \exp(-\Delta H' / (1+m)RT) t^{\frac{1}{m+1}} \quad (4-12)$$

By comparing Eqn 4-12 and 4-3, we can determine the relationship between A₀ and A', ΔH and ΔH', time exponent n and m, since Eqn 4-12 is analogous to Eqn 4-3 to express the IMC growth for isothermal aging. By substituting A, ΔH and n into Eqn 4-12, the IMC growth subject to any temperature profile after any aging time can be predicted as,

$$x_t = x_0 + \left[\frac{1}{n^2} A_0^n \int_0^t \exp(-\Delta H / nRT) dt \right]^n \quad (4-13)$$

Since n, A₀, ΔH is determined from isothermal aging experiments; Eqn 4-13 can be used to calculate the IMC layer growth for any TC aging profile.

The calculation of IMC thickness subject to TC aging by Eqn 4-13 can be integrated over a short-period or long-period thermal cycling profile. To simplify the calculation of IMC growth for thermal cycling, we can define an effective time t_{eff} , so that the IMC thickness can be estimated by Eqn 4-14,

$$x_t = x_0 + A_0 t_{eff}^n \exp(-\Delta H / RT) \quad (4-14)$$

Comparison between Eqn 4-13 and Eqn 4-14 gives the value of t_{eff} . For most commonly used TC aging profiles, t_{eff} , roughly equals to the total time at upper soak temperatures. Three thermal cycling profiles are shown in Table 4-3. The calculated IMC thickness for these three thermal cycling profiles is given in Table 4-4. The approximate model results calculated by Eqn 4-14 and the integration model results by Eqn 4-13 were derived from the IMC layer growth data for SAC387/ENIG solder joint results mentioned in this chapter.

Table 4-3 Thermal cycling aging profile, TC (thermal cycling), TS (thermal shock)

Test	Temperature	Cycle time	Ramp rate	Soak time
	range	(min)	(°C /min)	At max. & min. Temp. (min)
TC	- 40 to 125°C	56	≈12.7	15
TS	- 55 to 125 °C	17	≈ 51.4	5
Long TC	- 40 to 125°C	200	≈2.06	20

Table 4-4 IMC layer thickness prediction for SAC387/ENIG reaction couple, by approximation (Eqn 4-14) and integration (Eqn 4-13)

Number of cycles		500	1000	2000	3000	Error
X(TC)	Approximation	2.24	2.62	3.15	3.56	2%
(μ m)	Integration	2.27	2.66	3.21	3.64	
X(TS)	Approximation	1.85	2.07	2.38	2.62	1%
(μ m)	Integration	1.86	2.09	2.40	2.64	
X (Long TC)	Approximation	2.38	2.82	3.43	3.91	20%
(μ m)	Integration	2.70	3.26	4.07	4.68	

It can be seen that when the phases of ramp up and ramp down are not too slow

(e.g. comparable period with TC and TS condition), the approximation error is only about 1-2% when using total time at upper soak temperature as t_{eff} . Eqn 4-14 shows that the aging at upper soak temperature is the major contribution in one thermal cycle for TC and TS profiles and Eqn 4-14 can be used compared to Eqn 4-13 to predict the IMC layer thickness with 1-2 % error. However for the long-TC profile case with a cycle time of 200 minutes, ramp rate of 2°C/min, and a soak time of 20 minutes the error margin increases to 20 % and the integrated IMC layer growth model given by Eqn 4-13 is needed to model the cumulative IMC growth effect over the whole Long-TC cycle. The simple model using Eqn 4-14, assuming only the peak dwell time at 125°C contributes to IMC growth under predicts the IMC layer thickness significantly. In service operation conditions, the thermal cycling period is even much longer than 200 minutes, hence the integrated model for predicting IMC layer growth using Eqn 4-13 is highly relevant.

4.5.2 IMC Growth in One Temperature Cycle

The integral IMC growth model given by Eqn 4-13 can be used for any non-isothermal aging, besides the thermal cycling aging. The coefficients can be determined from the growth model for isothermal aging, and for the case of SAC on ENIG (NiAu) surface finish in this study, the IMC growth rate is,

$$v = \frac{dx}{dt} = 4.42 \frac{1}{x} \exp(-142.9 \times 10^3 / RT) \quad (4-15)$$

After certain period of thermal cycling aging, the corresponding NiCuSn ternary IMC thickness for SAC387/NiAu is,

$$x_t = (1.35 \pm 0.2) \times 10^{-6} + 2.97 \times \left[\int_0^t \exp(-142.9 \times 10^3 / RT) dt \right]^{0.5} \quad (4-16)$$

The total IMC thickness growth after 500, 1000, 2000 cycles can be calculated cycle by cycle using Eqn 4-16. Consider the IMC growth procedure in one cycle, the IMC growth rate v is affected by temperature change. Take TS aging as example:

At 125 °C, for 5 minutes,

$$v_{125} = \frac{1}{x} 4.42 \exp(-1.43 \times 10^5 / 8.31 \times 398) = 7.38 \times 10^{-19} \frac{1}{x} m / sec \quad (4-17)$$

At -55 °C for 5 minutes,

$$v_{-55} = \frac{1}{x} 4.42 \exp(-1.43 \times 10^5 / 8.31 \times 218) = 2.31 \times 10^{-34} \frac{1}{x} m / sec = 3.13 \times 10^{-16} v_{125} \quad (4-18)$$

At the ramp from -55 to 125 °C and reverse, 3.5 minutes each:

$$v_{ramp} = \frac{1}{x} 4.42 \exp(-1.43 \times 10^5 / 8.31T) m / sec \quad (4-19)$$

The NiCuSn IMC growth rate v_T/v_{125} subject to time in one cycle is plotted in Figure 4-10. It can be seen that during the ramp period, v_{ramp} drop to a very low value, quickly. In the lower soak temperature -55 °C, the value of V_{-55} is only 3.13×10^{-16} times of V_{125} . The diffusion at lower temperature can be ignored compared to the contribution at higher temperature. So it is reasonable to assume that only the upper soak temperature segments at 125 °C of the cycles contributes to the IMC layer growth and the growth is negligible at other segments and can be neglected.

Figure 4-10 IMC growth rate subject to time in one TS aging (◆) temperature, (■) IMC growth rate

The IMC growth procedure for TC and TS aging can be estimated by Eqn 4-14. The effective aging time, t_{eff} for TC and TS, can be simply defined as the total accumulated dwell time at 125°C. For TS aging between -55°C to 125°C, the cycle time is 17 minutes and the dwell time at the upper soak temperature is 5 minutes. Thus the t_{eff} for 2000 cycles of TS aging is 10,000 minutes or 600,000 seconds.

The calculation of IMC growth for TC and TS can employ Eqn. 4-14. The time exponent has been determined to be 0.5, the NiCuSn IMC growth is proportional with the square root of time. The IMC thickness for isothermal aging, TC and TS aging at 125 °C, x_t , can be described by,

$$x_t = x_0 + D\sqrt{t} \quad (4-20)$$

where D is the diffusion coefficient, the combination of constant A and the temperature factors; x_0 is the initial IMC thickness and t , for isothermal aging, the total aging time. The diffusion coefficient is given by an Arrhenius expression,

$$D = D_0 \exp(-\Delta H / RT) \quad (4-21)$$

where D_0 is the diffusion constant; ΔH is the apparent activation energy (kJ/mol). R is universal gas constant, and T is the absolute temperature (K). The values of $D_0 = A = 4.92$, and $\Delta H = 72.9$ kJ/mol for NiCuSn IMC growth, which was determined from isothermal aging.

4.5.3 Comparison of Isothermal, TC and TS Aging

In the previous sections, the IMC growth model for TC and TS was discussed by assuming that the growth mechanism for non-isothermal are not affected by the stress effect during the temperature cycle. However, it is possible that other growth mechanisms were included during the non-isothermal aging, for example, thermal stresses generated during the thermal cycling aging accelerate the diffusion and the IMC growth.

The IMC thickness measured for TC, TS and isothermal aging at 125°C are plotted in Figure 4-11. The aging time for TC and TS is the dwell time at the upper soak temperature of 125 °C. It is interesting to note that the IMC growth rates for TS and TC aging are higher than isothermal aging. The relationship shows that the IMC growth for TS aging is faster than TC aging and TC aging is faster than isothermal aging. This may be due to higher thermal stress-strain effects generated from non-isothermal TC and TS aging conditions, which can accelerate the IMC growth process. The effect of TS aging on IMC growth rate is greater than TC aging, suggests that

stress relaxation in the solder joint is not as pronounced in TS aging compared to TC aging which has a longer cycle time and soak period. For isothermal aging at 125°C, however, it allows for extensive stress relaxation in the solder joint, giving lower stress and hence lower IMC growth rate.

Figure 4-11 Comparison of IMC data for TC, TS and Isothermal Aging at 125 °C
(♦)ISO 125, (■)TC, (▲)TS

4.5.4 Acceleration Factor K

To quantitatively represent the thermal stress-strain effect for TC and TS aging, another parameter “equivalent isothermal aging time” t_{eq} is defined to calculate the time required by isothermal aging to obtain the same IMC thickness with TC or TS. For example, after 2000 cycles of TC aging, The IMC thickness accumulated x_t is 3.5 microns. To obtain such an IMC thickness by isothermal aging, it will need an equivalent time, t_{eq} , of 694 hrs, which is calculated by Eqn 4-22. It is directly derived from Eqn 4-20.

$$t_{eq} = \frac{1}{D_{125}^2} (x_t - x_0)^2 \quad (4-22)$$

By comparing the previous defined “effective aging time” t_{eff} and t_{eq} , it can be seen that t_{eff} is shorter than t_{eq} , for example, the t_{eff} for 2000 cycles of TS aging is 500 hrs, while t_{eq} is 694 hrs. This indicates that thermal stress-strain effect caused by temperature cycling accelerated the IMC growth rate.

In accelerated tests such as TC and TS are commonly used, an accelerated factor, AF, is then needed to relate the accelerated test and service operation. Similarly, the acceleration factor K is defined here to represent the scale factor that TC and TS have in accelerating the IMC growth compared to isothermal aging. The value of K, is defined as the ratio of t_{eq} divided by t_{eff} , as expressed in Eqn 4-23. For TC at 2000 cycles, the accelerated factor is 1.39.

$$K = \frac{1}{D_{iso}^2 t_{eff}} (x_t - x_0)^2 \quad (4-23)$$

The t_{eq} and the accelerated factor for each TC, TS aging were calculated and shown in Table 4-5. After 2000 cycles of TC and TS aging, the factor K is 1.39 and 2.24 respectively. This suggests that both TC and TS aging accelerate the growth of IMC and reflects the effects of thermal stress-strain effect on IMC growth.

Table 4-5 Equivalent isothermal aging time considering the IMC growth for TC&TS

Process condition	effective time t_{eff} (hrs)	IMC Thickness x_t (microns)	Equivalent isothermal time t_{eq} (hrs)	Accelerated factor $K=t_{eq}/t_{eff}$
500 TC	125	2.42	172	1.38
1000 TC	250	3.42	643	2.57
2000TC	500	3.5	694	1.39
500 TS	41.7	2.1	84	2.01
1000 TS	83.3	2.61	238	2.85
2000 TS	166.7	2.93	375	2.24

4.6 THERMAL CYCLING FATIGUE FAILURE ANALYSIS

4.6.1 In-situ Digital Image Speckle Analysis (DISA) Measurements

Digital image speckle analysis (DISA) was used to characterize strain distribution in a solder joint [113]. Fig. 4-12(a-c) shows the images captured at room temperature (25°C), 75°C and 125°C by Micro-DISC system. The bottom of the figure is the board side of the assembly. The location of the solder ball is A1, as indicated in Fig 4-2. These three images were used for displacement and strain analysis with the DISA. The image at room temperature is taken as reference image for comparison.

Figure 4-12 LSM images of solder joint “A1” during thermal loading

Fig 4-13(a-f) shows the displacement and shear strain field for 75°C and 125°C, respectively. The U and V fields are displacements in horizontal (x) and vertical (y) directions. For both temperatures, it shows that for the largest displacement for U field is located at the bottom right corner of the solder joint. The largest displacement for V field is located at the right corner of the solder joint.

The displacement patterns show that when temperature rise from 25°C to 75°C or 125°C, the displacement of the solder joint has horizontal translation and superimposed with a small bending rotation. This observation coincides with the common understanding of the deformation of packaging assembly. Fig 4-13(e-f) shows the derived shear strain fields from the corresponding displacement fields. As indicated in

Figure 4-13(e), the largest shear strain (in absolute value) at 75°C is about 0.52%, and located near the top left corner of the solder ball. The overall shear strain is around 0.15%. While for the shear strain at 125°C shown in Fig 4-13(f), the largest shear strain (in absolute value) is about 1.4%, and the overall strain is around 0.4%.

Figure 4-13 Displacement and shear strain fields solder ball “A1” at 75°C, 125°C from DISA correlation 75°C: (a)U field; (c)V field; (e)shear strain, ϵ_{xy} ; 125°C: (b) U field; (d) V field; (f) shear strain, ϵ_{xy}

The DISA measurement was conducted on the solder ball I9, which located beneath the silicon die, as shown earlier in Fig 4-2. Fig 4-14 (a-b) shows shear strain field, which is determined by DISA analysis at 25°C, 75°C, 125°C. Only the shear strain field is the major concern in reliability analysis and is presented. the displacement fields were not presented. Comparing I9 to the solder A1 at 75°C, the shear strain fields for I9 is larger in general. The largest shear strain (in absolute value)

at 75°C is about 0.94%, and is located near the left corner of the solder joint. The largest shear strain at 125°C is about 1.7%, as shown in Fig 4-14(b). This is higher than the strain at solder joint A1, 0.8%. The CTE mismatch at solder joint I9 is higher than that at solder joint A1 due to the existence of the silicon die.

Figure 4-14 Shear strain fields solder ball “I9” at 75°C, 125°C from DISA correlation

4.6.2 Thermal Cycling Lifetime Characterization

Thermal cycling test were conducted on 5 PCB test boards. A daisy chain is connected to monitor the resistance change of all the solder joints (in series). The initial resistance is about 2 Ohm. When the chain resistance increased to 300 Ohm, the computer program automatically records the cycles to failure. The failure data was fitted to two-parameter Weibull plot. The Weibull parameters for characteristic life and slope are given in Table 4-6.

Table 4-6 Thermal fatigue life for PBGA316, with SAC387/ENIG solder joint

Cycles to failure	Weibull parameters		
	Slope (β)	Characteristic. Life (η)	MTTF
2131,2745, 2892,2972, 3053	7.69	2917	2742

The cumulative distribution of failures, or the possibility to failure before cycle number, $F(N)$ can be expressed as Eqn 4-24. The characteristic life (η), and slope or

shape parameter (β) can be determined by Eqn 4-24.

$$F(N) = 1 - \exp \left[- \left(\frac{N}{\eta} \right)^\beta \right] \quad (4-24)$$

With the limited test data (only 5 PCB were available), the characteristic life can be determined, as 2917 cycles. The mean time to failure (MTTF) is 2742 cycles.

4.6.3 IMC Growth at Different Locations in PBGA

The thickness of IMCs after 3000 thermal cycles was observed by SEM for the solder joints at different location. The IMC thickness data for row A, C, E, G, I, K are plotted and shown in Figure 4-15. The IMC layer thickness at different solder joint locations are different after the 3000 thermal cycles of aging.

For solder joint at row A, C and E, the highest IMC layer thickness was found at the outmost solder balls. In row A, the IMC thickness decreases from A1 and A20 to the center balls A10. The average IMC thickness is 4.6 microns at A1 (or A20) and 4.2 microns at the center solder ball A10 (A11). Similar trend were noted for row C and row E. For row G, I and K; IMC thickness for all solder balls show a flatter trend for outer to center solder ball. It is noted that the materials adjacent to solder ball are different, causing different CTE mismatch and stress on the interface between solder and substrates.

By using the concept of “equivalent isothermal aging time” and “acceleration factor K” proposed in section 4.5, the IMC growth rate subject to TC can be compared with isothermal aging. The equivalent isothermal aging time for 3000 thermal cycles is 750 hrs at 125 °C (assuming only the upper soak temperature accounts for IMC layer growth). The acceleration factor K, for different solders, ranges from 1.2 to 1.7. From these data, it can be seen that the IMC layer growth is location dependant when the

PBGA is subject to TC aging. This suggests that thermo-mechanical stress generated by CTE mismatch during temperature ramp and dwell accelerated the IMC layer growth.

Figure 4-15 IMC layer thickness respect to locations of solder balls at row A, C, E, G, I and K

4.6.4 Crack Formation and Failure Analysis

After the TC tests, the PBGA assemblies were cut out, mounted, cross-sectioned and observed by SEM. Fig. 4-16 shows the cross-sectional image of a typical solder

joint fatigue failure for solder ball I9. The observed failure mode is fatigue cracking adjacent to the solder interface in the solder materials at the package side, primarily. Secondary cracks occurred at board side as well.

Figure 4-16 The SEM images of solder joint failure sites

Fig 4-17 shows component side solder joint failure location at the diagonal solder joints of A1, B2, C3, D4, E5 and I9 respectively. Cracks occurred near the intermetallic-to-solder interface (solder side). In the outermost joints A1, crack propagates from the both side and almost fractures through the joint width. For the solder joint underneath silicon die, the joint I9 has already failed. The crack behavior for solder joint B2, C3 and D4 shows early crack propagation. No cracking was observed for E5. The failure sites and the stage of cracks agree with the strain levels measured by DISA in section 4.6.1. Faster crack growth occurred at the solder joint with higher shear strain.

Figure 4-17 Interfaces at the component side of solder balls in diagonal of BGA

4.7 SUMMARY

The IMC growth kinetic for lead-free SAC solder interface subject to isothermal and thermal cycling aging were compared for different solder/substrate interfaces. An integration model was developed for calculating of the IMC growth for different thermal cycling aging profiles. An approximate method assuming that the major contribution of IMC growth during thermal shock and thermal cycling aging comes from the upper soaks temperature (125°C) is satisfactory for the typical TS and TC aging profiles. Acceleration factor K is proposed to correlate the IMC growth for TC and TS with isothermal aging. For thermal cycling study on PBGA specimen, higher strain levels were observed at solder joint A1 and I9. The strain concentration at the corner of the solder joint caused the initialization of fatigue crack. SEM investigation

shows that the failure site corresponds with the higher strain levels measured by DISA. Earlier crack growth occurred at the solder joint with higher shear strain level. The IMC layer thickness at different solder joints in PBGA assembly varies with location after thermal cycling aging. The highest IMC layer thickness was observed at the outermost solder joint. Thermal stress effect generated by CTE mismatch during temperature cycling accelerate IMC growth rate. Although thermal cycling aging caused IMC layer growth, the fatigue crack path is still in the solder and close to the interface. So the impact of needle-like (SAC/ENIG) or scallop IMC (SAC/Cu) on performance of solder joint subject to TC aging is not too significant.

CHAPTER 5 NANO-INDENTATION ANALYSIS

Nano-indentation characterization on SnAgCu (SAC) solder alloy, IMC and the substrate subjected to thermal aging are documented in this chapter. Modulus and hardness of thin IMC layers were measured by nano-indentation from the planar IMC surface. The creep effect on the measured result was analyzed when measuring SAC solder. The indentation strain-rate dependant hardness and elastic modulus was measured.

5.1 BACKGROUND

Nano-indentation measurement of modulus and hardness of the materials in lead-free assemblies have been reported [61-63,115,116]. The mechanical properties of lead-free solder joint, such as SnAgCu, SnCu, SnAg and the Intermetallic (IMC) formed between solder and substrate layer, Cu_6Sn_5 , Cu_3Sn and Ni_3Sn_4 were studied in literature [64-66,117,118]. Earlier works on IMC were done on bulk IMC specimens. In recent nano-indentation studies, the modulus, hardness and yield strength of interfacial IMC for solder joints were reported. SAC solder reflowed on electroless nickel and immersion gold (ENIG) surface finish generate a thin NiCuSn IMC layer which makes cross-section nano-indentation measurement difficult. Further, long-time reflow or aging for SAC/ENIG solder joint may affect the IMC composition, grain size and crystal orientation during IMC growth and thus their mechanical properties are subject to change.

For the indentation on most of the materials, it is known that a residual displacement of several nanometers occurs when the load is held constant after reaching the maximum load. The creep behavior depends on the materials and normally diminishes to very low value within some seconds. However, creep displacement for

solder alloy during nano-indentation is so significant to be able to reach several hundred nanometers during load-hold period. If creep is not considered, it can have a remarkable influence on the modulus and hardness result.

In this study, the effect of thermal aging on IMC mechanical properties was characterized from the planer IMC surface. Nano-indentation continuous stiffness measurement (CSM) technique was used to measure the IMCs' properties for SAC/Cu-OSP and SAC/ENIG specimens subjected to different thermal aging time. The creep effect on the indentation measurement for SAC solder and the relationship between indentation strain rate versus hardness is investigated. Finally the modulus and hardness of all the materials in the lead-free SAC solder joint were determined by nano-indentation CSM technique.

5.2 EXPERIMENTAL PROCEDURE

Lead-free PBGA (35x35mm) with 316I/O specimens were used in this study. The BGA solder joint specimen was prepared by solder reflow process. Lead-free solder balls 95.5Sn-3.8Ag-0.7Cu were soldered onto PCB board with Cu-OSP or ENIG surface finish. The reflow time above the melting point 217°C was 120 seconds. For ENIG surface finish, the Ni layer above Cu pad is 5 µm thick and the immersion gold layer is about 0.05-0.1 µm. Isothermal aging at 125 °C was conducted for solid state IMC growth up to 500 hrs. Upon completion of thermal aging, some solder joints were cut out from the PBGA assembly, mounted, cross-sectioned and polished for indentation on SAC solder. Some other solder joint specimens were selectively etched using 13vol % nitric acid, by which SAC solder was removed and IMC interface was exposed. The IMC surface was then slightly polished by the alumina suspensions until a flat IMC surface was obtained. Indentation test was conducted on these flat surfaces

by an instrumented MTS indentation XP system with a Berkovich tip. IMCs of as-reflowed, 260 and 500 hrs aged specimens were tested, respectively. Finally the specimens were observed by scanning electron microscopy (SEM).

Figure 5-1 Schematic diagram of conventional loading cycle and the CSM loading cycle, the way to determine contact stiffness is different in two methods

The hardness and modulus of IMCs reported in this study were the average value when displacement into surface is from 100 to 300 nm. The calculation of elastic modulus and hardness for nano-indentation CSM was based on the Oliver and Pharr Method [69]. The difference for CSM and conventional method is how contact stiffness (S) was obtained [68]. Figure 5-1 shows the schematic load-displacement diagram of CSM and conventional methods. For conventional nano-indentation, stiffness is the differentiation of load over penetration at the maximum depth of the unloading curve, For CSM, stiffness is determined by the harmonic oscillating force and the displacement response of the indenter superimposed onto the nominally increasing load.

During the measurement, the contact stiffness is output continuously from the nano-indentation system. For each specimen, 15 points (3x5 arrays) were tested. The selection of position to indent could be controlled under a high resolution optical microscope, by which various IMCs and Cu or Ni substrate could be recognized by

their colors. Further, since the elastic modulus and hardness for IMCs, Cu and Ni substrate are different, curves for IMCs could be distinguished from the test array.

5.3 INDENTATION ON PLANAR IMC SURFACE

5.3.1 Preparation of Planar IMC Surface

In this section, the measurements of modulus and hardness of IMCs are discussed. Using nano-indentation CSM technique, both elastic modulus and hardness could be obtained continuously. Fig. 5-2(a-b) show the planar IMC surface microstructure of the as-reflowed samples. After selective etching to remove the SAC solder, the IMCs layer was exposed for investigation. The scallop-type IMC observed in Fig. 5-2(a) is typically Cu_6Sn_5 (or called η -phase) generated at the SAC/Cu reaction couple during solder reflow. When the reaction couple experienced long time thermal aging, a Cu_3Sn (ϵ -phase) layer formed between Cu substrate and η -phase. In Fig. 5-2(b), the needle or rod type IMC is typically NiCuSn ternary IMC phase generated at the SAC/Ni reaction couple. It was reported that crystal structure of NiCuSn ternary IMC is sensitive with the concentration of Cu in SAC. Change of 0.2Cu% by weight may shift the IMC from $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ to $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$. XRD, EPMA and phase theories were used to determine the structure [67,101,119].

Figure 5-2 Intermetallic viewed from planar surface (a) Cu_6Sn_5 (b) NiCuSn

The representative nano-indentation on the planar IMC surface of SAC/Cu and SAC/Ni(Au) samples is given in Figure 5-3. After selective etching, the IMCs were slightly polished mechanically until a flat IMC surface was obtained. The polishing process was carefully done to make sure that not too much of the IMC layer was removed. For tests on the planar surface, a test array of 5x3 indents was used with pitch of 30 μm . Indentations were made on IMCs surface after different thermal aging time.

Figure 5-3 Planar IMC surface indentation on IMC surface (a) Cu_6Sn_5 ; (b) NiCuSn

5.3.2 Nano-indentation CSM Measurement

The representative test curves for Cu_6Sn_5 and NiCuSn are shown in Figure 5-4. The load-displacement curves are shown in Figure 5-4(1a, 2a). The curves for Cu_6Sn_5 before and after aging were roughly identical, thus only one curve for 500 hrs is presented. The elastic modulus, as a function of depth, is shown in Figure 5-4 (1b, 2b). The value of modulus becomes “stable” when the displacement increases to 50-100 nm. The hardness is shown in Figure 5-4 (1c-2c) for Cu_6Sn_5 and NiCuSn, respectively.

(1) Cu_6Sn_5 (2) NiCuSn

Figure 5-4 Load, modulus and hardness versus displacement curves for interfacial IMCs (a) Load vs displacement, (b) modulus vs displacement, (c) hardness vs displacement

5.3.3 Thermal Aging Effect on IMC Properties

A summary of the elastic modulus and hardness for the two IMCs subjected to thermal aging is shown in Figure 5-5. Elastic moduli of Cu_6Sn_5 after 0, 260 and 500 hrs thermal aging were found as 95.7, 97.0 and 97.4 GPa, respectively. The hardness values

were 6.09, 5.67 and 5.77 GPa respectively. This suggested that the modulus and hardness values do not change significantly with increase in IMC layer thickness.

Figure 5-5 Change of modulus and hardness versus thermal aging time at 125 °C

Reported results for Cu₆Sn₅ modulus show some variability from 85 GPa to 135 GPa [116-119], Deng et.al. [65, 66] measured the modulus of Cu-Sn IMC by nano-indentation on cross-sectioned solder joint specimen. The Sn-Ag/Cu sample was aged at 300 °C for 2 weeks to get a thick Cu₃Sn layer of 50 μm and Cu₆Sn₅ of 100 μm. This was done to ensure that the indents lie completely within each IMC layer. The modulus values for Cu₆Sn₅ and Cu₃Sn are 112 GPa and 134 GPa, respectively, which is higher than this study. Deng et al compared the results from literature and proposed that the elasticity anisotropy of hexagonal Cu₆Sn₅ contributes to the variability. In this study, the conditions used to fabricate the solder joints were similar to standard solder reflow parameters and the measurement direction was perpendicular to the direction used in previous work. It is believed that the IMCs at the interface may grow in some preferred orientations and thus lead to texture structure. Measurement in the directions vertical or parallel to the solder/substrate interface would yield different values as compared to polycrystalline bulk samples.

The change in modulus and hardness for NiCuSn layer at SAC/Ni couple was observed as shown in Fig. 5-5(a). The modulus measured from as-reflowed, 260 and 500 hrs aged specimens were 206.8, 164.9 and 145.8 GPa, respectively. The measured hardness were 10.07, 8.65, 7.31 GPa, respectively. The NiCuSn IMC decreases in modulus and hardness with thermal aging. Electron probe micro analysis (EPMA) was used to quantitatively determine the composition of NiCuSn IMC before and after thermal aging. It was found that for as-reflowed IMC, the compound was $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$ with 12atom% Ni. This is consistent with Chen's results [101]. After thermal aging of 260 hrs, the compound was still $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$, but the atomic percentage of Ni increased from 12% to 18%. After 500 hrs, however, the compound was found to be $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$. The modulus and the corresponding composition of the IMC are given in Table 5-1. It can be seen that the existence of Ni in NiCuSn affect the mechanical property significantly. For example, although Cu_6Sn_5 and $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$ have same crystal structure (hexagonal structure), the modulus of $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$ with Nickel substitution is almost two times higher than Cu_6Sn_5 . More Ni causes the crystal structure to shift from $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$ to $(\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4$, as elastic modulus decrease to about 140 GPa, while Ni_3Sn_4 and $(\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4$ have similar modulus.

Table 5-1 Comparison of Modulus of Cu-Sn, NiCuSn IMC

Phase	Solder Joint Type	Condition	Modulus(GPa)
Cu_6Sn_5	SAC/Cu	as-reflowed	97.0 ± 3.0
$(\text{Cu}_{0.78}\text{Ni}_{0.22})_6\text{Sn}_5$	SAC/Ni(electroless)	as-reflowed	206.8 ± 5.5
$(\text{Cu}_{0.67}\text{Ni}_{0.33})_6\text{Sn}_5$	SAC/Ni(electroless)	260 hrs, 125 C	164.9 ± 3.1
$(\text{Ni}_{0.51}\text{Cu}_{0.49})_3\text{Sn}_4$	SAC/Ni(electroless)	500 hrs, 125 C	145.8 ± 3.3
Ni_3Sn_4	SnAg/Ni	--	130-150

5.4 CREEP EFFECT ON INDENTATION MEASUREMENT

5.4.1 Load-displacement Curve

The indentation study on cross-sectioned SAC solder alloy was investigated. The creep phenomena and the corresponding effect on measurement of hardness and modulus were studied. The effect of solder creep on measurement were observed by applying a load onto the indenter tip at a constant loading rate and then the load were held at the maximum for a period. The loading rate used were, 0.1, 0.17, 0.33, 2 and 10 mN/s, each to a maximum load of 10 mN. The load ramp was immediately followed by a load hold period, during which the further displacement was observed. The hold time under constant load was 400 seconds.

Figure 5-6 Indentation load of 10 mN with different load rate

The load-time curve with different load rates from 10 to 0.1 mN/s is given in Figure 5-6. For typical materials without creep effect, the corresponding load-displacement curve should be identical and not significantly affected by load rate. However, the displacement response for SAC solder alloy was different, as shown in Figure 5-7. When load rate decreased from 10 to 0.1 mN/s, the displacement into surface increased. For example, with the same load of 6 mN during the increase, the

displacement was 1200 nm when the load rate was 0.1 mN/s, while it was only 800 nm for load rate of 10mN/s. At the maximum load of 10 mN, the difference of displacement could be as large as 500 nm between load rate of 0.1 and 10 mN/s.

Figure 5-7 Indentation displacement into sample at different load rate on SAC alloy

5.4.2 Hardness-displacement Curve

The hardness-displacement curve where the hardness was defined as the instantaneous mean pressure on the surface, can be calculated with load divided by the projected contact area, as shown in Figure 5-8.

Figure 5-8 Comparison of hardness-displacement curve with different loading rate from 0.1 mN/sec to 10 mN/sec, to the maximum load of 10 mN

It can be seen that the nominal hardness vary with test condition. For an indentation with constant load rate, 2 mN/s, for example, the initial hardness was about 0.35 GPa and gradually decrease to 0.27 GPa, also at the load hold period, the nominal hardness continue to decrease due to the creep displacement. For different load rate, hardness is load-rate-dependant, higher load rate produce higher measured hardness value due to strain-rate hardening effects.

5.4.3 Displacement at Load Hold

The nano-indentation tests with different maximum loads from 6, 10 to 20 mN were conducted. For each test, the time to maximum load was kept the same at 30 seconds. Then the load was held at the maximum value with a period of 400 seconds. The representative indentation marks for 6 mN, 10 mN and 20mN are shown in Figure 5-9.

Figure 5-9 Nano-indentation marks array with different load

The corresponding displacement vs time curve with the starting point at the beginning of hold period was shown in Figure 5-10, it can be seen that the displacement continues to increase and higher load caused larger displacement. It seems that displacement rate slow down with an exponent relationship. For many investigated

materials, the shape of the curve displacement-at-hold-period can be described with the well known logarithmic creep behavior [120],

$$\Delta h = A \ln(Bt + 1) \quad (5-1)$$

where t is the hold time, Δh the displacement increment at the maximum load and A,B are fit parameters. However, it is noted that Δh in Fig 5-10 is also load-rate dependent; in which different load-rate will yield a different starting point to calculate Δh . From the observation above, it can be seen that the indentation displacement is test-condition dependent, it is difficult to define a meaningful and comparable hardness for SAC solder alloy from nano-indentation. A suitable test method is required, by which the hardness could correlate with loading method.

Figure 5-10 Displacement increment during hold period with 6, 10 and 20 mN

Further indentation was performed to study the effect of creep on measurement of elastic modulus. For elastic materials, indentation depth will become stable in several seconds when the test reach the maximum load, but for SAC solder alloy in this study, it was found that displacement continues due to creep for a long time and the penetration depth could increase by up to 1 μm when the load was held constant at

several mN. It influences the maximum depth and the upper part of the unloading curve and can cause measurement errors of modulus by more than 50%.

The unloading curves after different holding time were compared at the upper region as shown in Figure 5-11. The unloading curves begin at higher depths for longer hold periods. It can be clearly seen that the unloading curve shows a bowing towards higher depth if the hold period is too short. The penetration rate within the first 5 sec after reaching the maximum load was about 6nm/sec, while the unloading rate was only approximately 2nm/sec for the whole unloading curve. However, after a hold period of 100 sec the creep rate is reduced to about 0.3nm/sec. Since the inclination of the unloading curve at maximum load is used for the calculation of the modulus, any bowing leads to a high modulus error. From this investigation in Figure 5-11, it is observed that by simply prolonging hold period to 100s or more, bowing towards higher penetration is eliminated.

Figure 5-11 Unloading curve after different hold time, bow-shape unloading curve was seen for a short hold time due to the creep effect

5.5 STRAIN-RATE-DEPENDANT HARDNESS

5.5.1 Controlled Indentation Strain Rate

The indentation strain rate ($\dot{h}/h$) also changes continuously within one test circle, during loading and the subsequent load-held segment. For the measurement of steady-state stress-strain rate curve from bulk SAC solder specimen, it has been well understood that the stress for a viscoplastic material is a function of applied strain rate and temperature, so the indentation hardness, or mean stress--should be expected to vary in an analogous way. Lucas et al.[121] proposed an indentation experiment to study the creep behavior of indium based alloy using Berkovich tip, during which the indentation strain rate and therefore, hardness remains constant. The indentation hardness of a material is given by,

$$H = \frac{P}{A} = \frac{P}{ch^2} \quad (5-2)$$

where H is the hardness, P is the load, A is the projected contact area, h is the displacement (contact depth), and c is a constant that depends upon the geometry of the indenter tip (for perfect Berkovich tip, c=24.56). Eqn 5-2 can be differentiated and simplified to obtain,

$$\frac{\dot{h}}{h} = \frac{1}{2} \left(\frac{\dot{P}}{P} - \frac{\dot{H}}{H} \right) = \dot{\varepsilon}_i \quad (5-3)$$

where $\dot{\varepsilon}_i (= \dot{h}/h)$ is the indentation strain rate. Eqn 5-3 suggests that an indentation experiment performed with a pyramid-shaped indenter, during which the loading rate is controlled so that the loading rate divided by the load ($\dot{P}/P$) is constant. This can result in a constant value of the indentation strain rate if a steady-state value of the

hardness can be reached and $\dot{H} = 0$. This is very important, as the loading rate is a program-controllable parameter in the MTS indentation XP system.

5.5.2 Power-Law Hardness-Strain Rate Relationship

To find the steady-state hardness at different indentation strain rate, a series of experiments at varying of $\dot{P}/P$ value were conducted. The loading rate was controlled in such a way as to maintain the instantaneous value of $\dot{P}/P$ constant till the indentation depth reaches 1000nm. The $\dot{P}/P$ values of 0.002, 0.02, 0.10, 0.2, 1.0 and 20 sec^{-1} were used. Figure 5-12 shows the indentation strain rate dependant load-displacement curve. For SAC solder, it shows that the higher strain rate, the higher load is required to achieve the same indentation depth.

Figure 5-12 Load versus displacement when indentation strain rate $\dot{h}/h$ is 0.001, 0.01, 0.1, 1, and 10 respectively.

A plot of hardness versus displacement for the loading method of constant $\dot{P}/P$ is give in Figure Figure 5-13. After a short transient period, the calculated hardness

become stable and is subject to the value of $\dot{P}/P$. As indicated in Eqn 5-3, if hardness becomes constant and $\dot{H} = 0$, the indentation strain rate ($\dot{h}/h$) equals half of $\dot{P}/P$. Since the constant $\dot{P}/P$ was used, $\dot{h}/h$ was also constant during the test. For example, when the value of $\dot{P}/P$ was 0.002, 0.02, 0.2, 2.0 and 20 s^{-1} , the corresponding indentation strain rate $\dot{h}/h$ was 0.001, 0.01, 0.1, 1 and 10 respectively.

Figure 5-13 Hardness vs displacement when the $\dot{P}/P$ was 0.002, 0.02, 0.2, 2 and 20 s^{-1} , the corresponding $\dot{h}/h$ was 0.001, 0.01, 0.1, 1 and 10, respectively.

Thus, for each $\dot{P}/P$ experiment, a corresponding constant $\dot{h}/h$ and H were achieved. “Steady-state” indentation strain rate vs stress (hardness) could be plotted as similar to conventional tensile test. Figure 5-14 shows the log-log plot of indentation strain rate vs hardness for the data from the constant $\dot{P}/P$ experiments.

Figure 5-14 Log-log plot of hardness vs indentation strain rate.

The hardness data were generated by averaging the constant hardness between 300 to 800 nm. A power-law fit to the data yields a slope of 0.15. At room temperature, the relationship between indentation strain rate and hardness could be expressed as,

$$H = K(\dot{\varepsilon})^n = K\left(\frac{\dot{h}}{h}\right)^n \quad (5-4)$$

where $K=0.3466$ is material constant, H is hardness, $n=0.1507$ is strain exponent. This strain exponent for indentation is consistent with reported value from uniaxial tensile test by Xiong [122]. The exponent value of 0.23 for bulk SAC 387 solder alloy at room temperature when the strain rate is at 10^{-5} to 10^{-2} . The reasonable range of strain exponent is between 0.1 to 0.3, depending on the materials composition and temperature.

5.5.3 Comparison of Yield Stress and Hardness

A simple estimation of the relationship between yield stress and hardness is given by, [123]

$$H = 3\sigma_y \quad (5-5)$$

The yield stress of SAC387 solder can be estimated at different strain rate using this method. The elastic modulus and yield stress was measured during the nano-indentation tests, and the result is given in Table 5-2. Compared with the tensile test results in Table 5-3 for the strain rate range from 10^{-3} to 10^{-2} , the elastic modulus and hardness from the two methods are comparable. The indentation yield stress for high strain rate of 1-10 1/s can be measured. For tensile test, the strain rate is often below 10^{-1} 1/s. The yield stress at ultra high strain rate [122] is also reported in the earlier study, which is determined by the Hopkinson bar test method. The yield stress at intermediate strain rates (1-10 1/s) is reported here for the first time.

Table 5-2 Summary of elastic modulus and yield stress from nano-indentation

Ind. Strain Rate	E (GPa)	Hardness (GPa)	Yield (H/3)
10^{-3}	51.15	0.129	43.0
10^{-2}	54.74	0.167	55.7
10^{-1}	58.26	0.249	83.0
1	62.3	0.352	117.3
10	~67	0.520	173.3

Table 5-3 Tensile Test Results for SAC Solder at room temperature [122]

	E (GPa)	Yield (MPa)
5.6×10^{-4}	41.8	35.1
5.6×10^{-3}	48.3	42.9
5.6×10^{-2}	55.1	52.8

At room temperature, the yield stress as a function of strain rate, can be curve-fitted as,

$$\sigma_y(\dot{\epsilon})_{SnAgCu} = 118.78(\dot{\epsilon})^{(0.1535)} \quad (5-6)$$

Figure 5-15 Schematic illustration of actual stress strain curves

The typical stress-strain curves is shown in Figure 5-15(a) from tensile test for SAC solder at different strain-rates. A simplified bi-linear model may be used to model the actual stress-strain curve, where the apparent elastic modulus and yield stress at different strain rates are available [122]. Thus bi-linear stress-strain curves can be generated for Finite Element Analysis (FEA) application using the data from Table 5-2, as shown in Fig. 5-15(b).

However, the difference between indentation and tensile test should be noted. The compression stress applied on the contact area is not uniform, especially the stress concentration at the tip end. Correlation between hardness and yield stress needs further studies. Dao et al. [124] proposed an empirical model to calculate the yield strength from the measured indentation curves, elastic modulus and hardness. However, the strain rate dependant behavior was not considered in the model, improvement to Dao's model will be useful to understand the indentation data on solder.

5.6 MECHANICAL PROPERTIES FOR SAC387 SOLDER JOINT

The elastic modulus for SAC387 solder joint in a 35x35mm PBGA assembly was determined by nano-indentation and given in Table 5-4. Both the conventional test

method and CSM method were used. The materials reported are, Ni(P) layer, NiCuSn IMC, Cu, Ag₃Sn, SAC1, SAC2, Cu₆Sn₅, Cu₃Sn and PCB.

Table 5-4 Modulus of different indentation site measurements in solder joints

Material	CSM	Conventional
	Elastic Modulus (GPa)	Elastic Modulus (GPa)
Ni(P)	204.5±1.7	180.4±12
*(Cu _{0.67} Ni _{0.33}) ₆ Sn ₅	164.9 ± 3.1	---
*(Ni _{0.51} Cu _{0.49}) ₃ Sn ₄	145.8 ± 3.3	---
Cu	114.5±2.2	104.5±4.1
Ag ₃ Sn	70.72±2.0	78.10±6.1
SAC387-1	43.05±1.58	45.2±5.1
SAC387-2	54.74±1.89	56.2±4.8
*Cu ₆ Sn ₅	96.73±0.36	92.6±2.3
*Cu ₃ Sn	114.8±1.3	102.7±3.1
PCB	5.88±0.11	6.30±0.25

* From planar IMC surface measurements

The solder joint was cross-sectioned for measurement. An indentation array test was conducted and some indents in solder were shown in Figure 5-16(a). After slight surface etching, two phases are seen in Figure 5-16(b). The dark phase in the figure is pure β -tin phase and the bright phase is eutectic phase, in which fine β -tin, Ag₃Sn and Cu₆Sn₅ exist together. Note that two groups of modulus and hardness values were observed. The average modulus for the first group is 43.05 GPa, which was indented on the β -tin phase(SAC387-1 in table 5-4); while for the second group, it is 54.74 GPa, which was indented on the eutectic phase(SAC387-2).

Figure 5-16 Indentations on pure tin and eutectic phases in SAC solder

It is reasonable that the eutectic phase has a higher modulus and hardness due to the “hardening” effect by small IMCs. The microstructure of solder ball was significantly different with bulk solder due to the cooling process in solder reflow. While for bulk solder alloy, the separation of eutectic and Sn-rich phases was hardly seen. The measured modulus for bulk SAC alloy was about 50GPa, it is actually the combined modulus of the two phases.

5.7 SUMMARY

Modulus and hardness of thin IMC layers were measured by nano-indentation from planar IMC surface. When SAC/ENIG solder joint were subjected to thermal aging, elastic modulus of the NiCuSn IMC at SAC/ENIG specimen changed from 207 GPa to 146 GPa with different aging time up to 500 hrs. The hardness decreased from 10.0 to 7.3GPa. For SAC/Cu-OSP reaction couple, elastic modulus of Cu_6Sn_5 remained constant at 97.0 GPa and hardness about 5.7GPa. EPMA shows the change of Ni and Cu concentration in NiCuSn ternary IMC during thermal aging, modulus for these ternary IMC and their correspond composition were determined. The indentation creep and the corresponding effect on measurement of hardness and modulus of SAC alloy were discussed. The indentation strain-rate dependant hardness was measured from

strain rate of 0.001 to 10 s⁻¹. The hardness of SAC change from 0.129 to 0.520 GPa respect to the strain rate.

CHAPTER 6 ELECTROMIGRATION EFFECT ON IMC GROWTH AND BACK STRESS IN SOLDER JOINT

In this section, the impact of Electromigration (EM) on the growth of interfacial IMC at anode and cathode side is demonstrated. The effect of EM induced back stress on atom transport was studied by an array of nano-indentation markers on cross-sectioned FPBGA specimen.

6.1 BACKGROUND

The size of solder joint used in electronic assemblies is becoming smaller and smaller. The solder ball bump size is 100 μm in feature size for flip chip assemblies and this is expected to reduce to 50 μm and below in the future. EM due to high current density has become a serious concern for packaging reliability [125]. The phenomenon of EM has been the subject of intense study. Both theoretical and experimental work has been reported [126-131]. High current density in integrated circuit interconnects causes a net movement of metallic atoms. The atoms generally migrate in the same direction as the electron flow. This leads to a continuous atom mass transport and cause atoms to pile up in the direction of the electron flow (anode) and produce voids in an upstream direction (cathode) with respect to the electron flow. These defects can lead to failures in integrated circuits [127]. In solder joints, the distribution of current density is far from uniform. The current density can be about one to two orders of magnitude higher than the average current density. At the joint corner, the current density can be 10^5A/cm^2 if the average value is in the order of $10^3\text{-}10^4 \text{A/cm}^2$. Voids can form and expand quickly at the solder joint corners. With these voids or crack growth, the non-uniformity of the current density over the solder joint increases further. Since the Joule heating is proportional to the square of the current density, the local temperature is also

much higher than average temperature. The current crowding effect therefore plays a double role here; both the elevated local current density and temperature accelerate the IMC growth and void formation. The impact of EM on SnPb and Pb-free solder joint was reported in previous studies [127-129]. For SnPb solder, the two-phase system experiences phases coalesce and phases segregation. For both SnPb and Pb-free solder joint, one of the major concerns is the EM effect of IMC growth at the anode and the cathode.

Pre-existed voids formed during soldering reflow are frequently found in solder joint even with many optimized materials and process. Compared with Sn–Pb solders, the reflow of Pb-free solder alloys requires higher temperatures. The boiling point of the flux is just 30 °C above the peak of Pb-free solder reflow profile, because the boiling point of tripropyleneglycol butyl ether which is the general solvent in solder flux is 276 °C. Therefore, any surface residue on the bond pads on the substrate side may promote premature liquid-vapor phase transition of the flux solvent below its boiling point. The entrapped vapor creates voids when the solder solidifies. The solder joint failure related to pre-existed voids is reliability concern. Experimental work to study how electromigration in solder joint interact with voids and cause final failure is not reported in literature. The major difficulty is the random size and distribution of voids in solder joint. Theoretical analysis on void migration is reported by Nah [132] in a recent study, two possible mechanism, rigid marker diffusion and atom diffusion on void surface are proposed, both of which will lead to the void move toward cathode, or against Sn atom flux. Experimental studies on the movement of embedded polishing diamond particles were reported for SnPb and Pb-free solders [133].

In this study, the impact of EM on the IMC growth for SnAgCu with different UBM couples was tested on Single BGA ball specimen and FPBGA specimen. The

IMC growth rate as well as the IMC composition was studied. The mechanical properties of the IMC at anode and cathode were measured by nano-indentation. EDX line scan analysis was conducted at the interface from anode to cathode. The effect of electromigration and back stress on the nano-indentation array markers movement at different location was observed. The back stress, stress gradient and effective charge number Z^* for SnAgCu solder are calculated observed.

6.2 EXPERIMENTAL PROCEDURE

The solder joint specimens, the electromigration test and interface morphology characterizations are discussed in this section.

6.2.1 Electromigration Test

The single BGA ball solder joint specimen consists of a single 95.5Sn-3.8Ag-0.7Cu solder (SAC) ball with diameter of 0.5mm and pad opening of 0.3mm, soldered between two FR4 substrate materials as shown in Figure 6-1.

Figure 6-1 Solder Joint Specimen, after reflow, the joint is Ni/SAC/Ni

The fabrication of the specimen was reported [103]. The ENIG surface finish on copper pad has a nickel (Ni) layer thickness of 5 microns and a gold (Au) flash thickness of 0.05 micron. The copper pad thickness is 30 microns. The FR4 substrate has dimensions of 12mm x 3mm x 0.5mm. The specimens are prepared using 8-zone

reflow oven. The solder reflow profile with a peak temperature of 250°C and time above melting point of 120 seconds was used in the fabrication.

Further study is conducted on FPBGA 324 I/O specimen, a daisy chain is designed to connect all the solder balls in series, by which thermal cycling and isothermal aging study were conducted [103]. A slice of BGA solder balls were cut from the whole assembly to conduct EM test as shown in Figure 6-2. The advantage of using slice specimen rather than the whole assembly is to avoid multiple failures in any one of the 324 solder joints and lower down the current heating. It was also noted that heat dissipation for slice specimen is better than using whole assembly.

Figure 6-2 Slice specimen cut from FPBGA and schematic of electron flow

EM test was performed on the solder joint specimen in a thermal chamber with isothermal temperatures of 125 and 150°C. To observe and calibrate the effect of joule heating, in-situ temperature measurement were conducted on slice FPBGA specimen before the sample was subject to combined thermal and EM exposure. Infrared thermal imaging system was used to determine the 2-D temperature distribution in solder joint interconnects. For EM test, the two enameled wires were connected to pass a constant

current, generating a nominal average current density of $5000\sim 10000\text{A}/\text{cm}^2$, calculation of current density is based on the area of the pad. The test time ranged from 1 day to 10 days with a tracking accuracy of 30 minutes. Isothermal aging for the specimen at the same ambient temperature was conducted for comparison.

6.2.2 Nano-indentation Marker Area Array

To study the movement of micro marker on cross-section of solder joint subject to electromigration, nano-indentation marker area array is created on cross-sectioned FBGA solder joint surface using an instrumented system MTS indentation XP with a Berkovich diamond pyramid tip. The solder balls are daisy-chained as shown in Figure 6-2. The position and depth of indentation marker is well controlled. Figure 6-3 shows the representative area array of nano-indentation marker created on the cross-sectioned solder balls, the depth of the marker shown in the figure is from $1\sim 8\text{ }\mu\text{m}$. The marker array was controlled at (a) $1\text{ }\mu\text{m}$ 5×6 +extra 4 markers at left and right, marker distance 65 microns: (b) $3\text{ }\mu\text{m}$ 4×5 +extra 3 markers at left and right, marker distance 75 microns and (c) $8\text{ }\mu\text{m}$ 3×3 , marker distance 140 microns. However, the size of the marker could be controlled down to as small as 50 nm.

Electromigration test was performed on the solder joint specimen in a thermal chamber with ambient temperature of 125°C . The two enameled wires were connected to pass a constant current generating a nominal average current density of $10000\text{A}/\text{cm}^2$ through the copper pad. The test time ranged from 1 day to 10 days with a tracking accuracy of 30 minutes. The EM test was monitored by an optical digital image system during the test. The direction of the electron flux for all the SEM pictures, if not stated, is from top to bottom respect to Figure 6-3. Upon completion of the aging treatment, the specimens were characterization using a JOEL JSM-5410LV Scanning Electron Microscopy (SEM) under an accelerated voltage 20kV.

Figure 6-3 Cross-sectioned solder joint with nano-indentation marker array

For investigation of the IMC layer at anode and cathode, digital imaging techniques were employed in the measurement of the average IMC growth thickness. Line scan composition analysis using Energy Dispersive X-ray (EDX) was conducted to character the composition distribution from anode to cathode in terms of the EM test. Quantitative composition analysis using Electron Probe MicroAnalysis (EPMA) was conducted on ENIG/SAC/ENIG specimen after EM. The mechanical properties of IMC before and after EM are measured by an instrumented system MTS indentation XP with a Berkovich diamond pyramid tip. The measurement is conducted from planar IMC surface. Solder joint specimens were selectively etched using 13vol % nitric acid, by which SAC solder was removed and IMCs interface was exposed. The IMC surface was then slightly polished by the alumina suspensions until a flat IMC surface was obtained. CSM Standard Hardness and Modulus test program was used with a depth limit into surface of 300-400 nm. The hardness and modulus of IMCs reported in this

study were the average value when displacement into surface increases from 100 to 300 nm. For each specimen, at least 7-10 points were tested.

6.3 IMC GROWTH AT CATHODE AND ANODE

During the EM exposure, both temperature and current density affect the reaction at the interface to form IMC. The IMC growth at the cathode and the anode are discussed in this section.

6.3.1 Joule Heating Characterization

Joule heating effect and current crowding accelerate the effect of EM in solder joints. It is necessary to measure the local temperature at solder joint during the accelerated EM test as temperature could be much higher than ambient. Figure 6-4 shows the temperature vs current density at cross-sectioned slice solder joint measured by Infrared thermal imaging system. The chamber background was set at room temperature (25°C) or 125°C. Temperature increase was observed on the solder joint compared to the ambient, the temperature increase at 125°C is higher than room temperature, this is reasonable as the resistance coefficient for SAC is higher at higher temperature, the heat generated would be more than in room temperature. For current density below 10^4 A/cm² in this study, joule heating cause a temperature increment of 10-30°C. It is noted that temperature increase for this specimen could reach 180 °C when the current density is about 4×10^4 A/cm² (solder was molten when ambient is 125°C). Thus higher current density studies were not conducted on this specimen.

Figure 6-4 Temperature increase vs current density at (a) corner (b) average

6.3.2 IMC Morphology at Anode and Cathode

The cross-section of the Ni/SAC/Ni single solder joint specimen before and after EM was shown in Figure 6-5(a-b); the direction of electron flow is as indicated. EM test at 150 °C on the single solder joint specimen with current density of 5,000 A/cm² after different exposure time up to 10 days was observed. Isothermal aging for the specimen at 150 °C was carried for comparison. Upon completion of the exposure, the specimens were cross-sectioned for investigation. Figure 6-5a showed the as-reflowed solder joint, in which the cross-sectioned interface was slightly etched after fine polished with 0.05 gamma alumina. The microstructure of the solder joint after reflow typically consist of globular Sn rich phases surrounded by small Ag₃Sn phases, and Cu₆Sn₅ are also present. Some large Ag₃Sn IMC rods are formed in the solder, and can be as long as 100 microns or more. Figure 6-5b shows the cross-sectioned morphology after EM exposure for 262 hrs, voids near the IMC layer and solder at cathode side were observed. Some irregular voids exist in the solder bump as indicated by the arrow. They should also form during the EM exposure as the pre-existed gassing voids are normally spherical in shape, due to the surface tension in molten solder/vapor interface. Hillocks at anode side was not seen in Figure 6-5(b) as the specimen was cross-section after EM test, the polished surface is flat.

Figure 6-5 Schematic of the EM test and the direction of the electron flow (a) 0h
(b) 260h

The NiCuSn ternary IMC growth at cathode and anode side with different aging time was observed. Figure 6-6 shows the interfacial morphology without EM exposure, the IMC on the solder/nickel interface are irregular and grow in needle like manner. The IMC layers at both sides are identical.

Figure 6-6 SEM image of IMC morphology for specimen without EM exposure

The SEM images after EM exposure up to 260 hrs at 150°C with current density of 5000A/cm² is given in Figure 6-7. It was observed that EM resulted in different IMC growth rate at anode and cathode side. NiCuSn ternary IMC at anode grow much faster than at the cathode side. After 49 hours of EM exposure Figure 6-7(a-b), both cathode and anode IMC become layer like, coalescence of the IMC needles leads to lateral thickening and ripening, the IMC thickness at anode is higher than cathode. The difference of thickness enhance as the current continuously apply on the sample. Some

interfacial voids could be seen at cathode side, as shown in Figure 6-7(c). Finally after 262 hours of EM test aging, the IMC thickness at anode increased to about $9\mu\text{m}$, while the Ni layer is almost consumed out. At the cathode side, the IMC thickness is about $5\mu\text{m}$. However, the IMC layer thickness at cathode is not uniform as voids form and can slow down the IMC growth. Subsequent coalesce of these voids can cause EM-induced solder joint failure.

Figure 6-7 Interfacial IMC morphology subject to EM at $5 \times 10^3 \text{ A/cm}^2$

Needle-like NiCuSn IMCs allow the direct contact between nickel and tin. Thus atomic interdiffusion caused faster IMC layer growth during electromigration. Ni(P) protective layer was consumed, which can cause voiding and embrittlement of Ni(P).

6.3.3 IMC Thickness Comparison

The IMC thickness at anode and cathode were measured using the digital imaging software, the result is compared to the IMC growth without current at 150 °C and 170 °C, is given in Figure 6-8.

Figure 6-8 Intermetallic growth thickness subject to current effect (▲) anode, electron $\text{Sn} \rightarrow \text{Ni}$ (■) cathode electron $\text{Ni} \rightarrow \text{Sn}$ (♦) Isothermal at 150 °C isothermal at 170°C.

The IMC at both anode and cathode side grow in thickness and faster than isothermal aging at 150 °C. The IMC growth on the cathode was supposed to be lower than isothermal aging at the same temperature as EM enhance the IMC dissolution at the cathode. However, considering the joule heating effect on the solder joint, it is noted that the actual temperature on the solder joint is higher than 150 °C. Joule heating effect should be removed in order to merely consider the effect of atom flux caused by EM. From Figure 6-4, it can be seen that the temperature increase at 150°C and 5000A/cm² for the solder joint in this study is about 20°C, as the IMC growth is both thermally activated and electrical accelerated. For comparison, the anode and cathode IMC growth should be compared with isothermal aging at around 170 °C.

Understanding the joule heating effect, we are able to identify the scale of the EM affects on the intermetallic growth. In order to simplify the comparison between the samples with and without current effect, the IMC growth was assumed to obey the parabolic IMC growth rate, by which the time exponent is 0.5. The IMC thickness, x , with and without current effect subject to the aging time can be calculated by,

$$x = D\sqrt{t} + x_0 \quad (6-1)$$

where D is defined as diffusion coefficient ($\mu\text{m}/\text{sec}^{1/2}$); x_0 is the initial IMC thickness and t is aging time. By using Eqn 6-1 to curve fit the IMC thickness as a function the square root of time as from IMC data in Figure 6-8, the diffusion coefficients is obtained and given in Table 6-1. The results for isothermal aging at 150 and 170 °C, D_{i150} , D_{i170} , cathode coefficient D_{c170} and anode coefficient D_{a170} are 0.082, 0.32, 0.18 and 0.47 respectively, where the unit for time is hour. Thus, $D_{i170} - D_{c170}$ is the dissolution coefficient caused by EM at 5000A/cm² at cathode, while $D_{a170} - D_{i170}$ is the elevatory coefficient. The diffusion constants here give the scale of the ions diffusion rate with and without the effect of EM. Chao et al [126] reported that the IMC growth rate follow a reaction controlled mechanism when the current density reaches 4x10⁴A/cm².

Table 6-1 Diffusion coefficients of the solder joint with and without EM

Symbol	Definition	Value at 170 C with current density of 5000A/cm ²
D_{i150}	Isothermal diffusion coefficient at 150°C	0.082
D_{i170}	Isothermal diffusion coefficient	0.32
D_{c170}	Cathode diffusion coefficient	0.18
D_{a170}	Anode diffusion coefficient	0.47
$D_{i170} - D_{c170}$	Dissolution coefficient	0.14
$D_{a170} - D_{i170}$	Elevatory coefficient	0.15

6.3.4 EM Effect on Solder with Cu-OSP and ENIG Surface Finish

Further IMC growth studies were observed on daisy chained FPBGA solder joints with Cu-OSP and ENIG surface finish at the board side. At the component side, the UBM is electrolytic Ni. The experimental setup was shown earlier in Figure 6-2. Five solder balls are selected in an FPBGA unit for applying current of $5000\text{A}/\text{cm}^2$ at 125°C . After 10 days, the solder joint interfaces were cross-sectioned for observation.

The direction of electron flow in sliced FBGA solder joints is shown in Figure 6-9. The electron flow in from top of the solder joint (1), goes through solder joint (1) and (2) along the route of (a)-(b)-(d)-(c). Location (a) and (d) are the cathode interface, (b) and (c) are the anode interface.

Figure 6-9 Daisy Chained solder with EM test at $5000\text{A}/\text{cm}^2$

Since the surface finish at board side (bottom in Figure 6-9, Cu-OSP or ENIG) and package side (top of Figure 6-9, electrolytic Ni) is different. Solder joints (1) and (2) show different IMC growth behavior. For the specimen with Cu-OSP, the interface morphology for the two solder joints is shown in Figure 6-10. (1) Electrolytic Ni/SAC/Cu where electron flux from Ni to Cu side. As shown in Figure 6-10(a-b), the growth of Ni-Cu-Sn layer at Nickel side was slow, but IMC growth at SAC/Cu side was slightly higher than isothermal aging. (2) Cu/SAC/electrolytic Ni where electron flux from Cu to Ni as shown in Figure 6-10(c-d), some Cu_6Sn_5 particles IMCs were

detected at the anode electrolytic Ni/SAC interface. This may indicate the migration of Cu from solder to the Ni/SAC interface.

Figure 6-10 IMC growth at electrolytic Ni/SAC/Cu-OSP solder joint with EM

For the specimen with ENIG surface finish at board side, the interface morphology for the two solder joints is shown in Figure 6-11. The solder joint (1) is Ni/SAC/ENIG where electron flows from electrolytic Ni to ENIG as shown in Figure 6-11(a-b). Voids were formed at the cathode Ni/SAC side, but not as significant as the case in (c).is and in solder joint (2) is ENIG/SAC/Ni where electron flux from ENIG to electrolytic Ni as shown in Figure 6-11(c-d), void can be seen near the IMC/SAC interface at the cathode ENIG/SAC side.

Figure 6-11 IMC growth at electrolytic Ni/SAC/ENIG solder joint with EM

6.4 EM EFFECT ON IMC COMPOSITION

The IMC composition at anode and cathode was examined using EDX and EMPA before and after EM test, the effect on mechanical properties, elastic modulus and hardness, are discussed in this section.

6.4.1 EDX Analysis of IMC

EDX line scan composition analysis was conducted from cathode to anode on the cross-sectioned solder joints. An example for ENIG/SAC/ENIG single ball solder joint was shown in Figure 6-12. The distribution and concentration of Cu, Ni and Sn are determined by their energy dispersive peaks $\text{CuK}\alpha$, $\text{NiK}\alpha$ and $\text{SnL}\alpha$, respectively. The intensity of secondary electrons (SE) is also shown in the figure.

Figure 6-12 EDX line scan of Cu, Ni and Sn species from cathode (left) to anode(right)
(1. Cu pad, 2. Ni layer, 3. cathode IMC, 4. SAC Solder, 5. anode IMC, 6. Ni layer, 7. Cu)

The local composition analysis on the anode and cathode IMC (with a distance of 15 μm) are shown in Figure 6-13. Although EDX line scan can not provide quantitative data, it is useful to determine the existence of species and compare the difference between anode and cathode.

Figure 6-13 EDX line scan of Cu, Ni and Sn species near (a) cathode and (b) anode

Table 6-2 IMC composition at anode and cathode for SAC with different surface finish

No.	Solder joint	Cathode IMC	Anode IMC
1	ENIG/SAC/ENIG	Ni, Cu, Sn (P)	Ni, Cu, Sn (P)
2	Electrolytic Ni/SAC/Cu	Ni, Cu, Sn	Ni, Cu, Sn
3	Cu/SAC/electrolytic Ni	Cu, Sn	Ni, Cu, Sn
4	Electrolytic Ni/SAC/ENIG	Ni, Cu, Sn	Ni, Cu, Sn (P)
5	ENIG/SAC/electrolytic Ni	Ni, Cu, Sn(P)	Ni, Cu, Sn

Note: electron is from the left to the right

The compositions in the IMC for different solder joint after EM exposure for 10 days are given in Table 6-2. The sample No.1 is for the ENIG/SAC/ENIG single ball solder joint and the followings are for FPBGA specimens. From the table, it can be seen that the species in IMC is related to local environment like solder composition and the corresponding metallic substrate. However, long distance atom electromigration seems to affect the IMC composition as well. For example in sample No.2, Ni atoms were detected in the IMC at anode SAC/Cu interface in electrolytic Ni/SAC/Cu solder joint. The Ni atoms could be only from electrolytic Ni at cathode side, it is confirmed that long distance migration of Ni from cathode to anode occurred. For comparison, Ni was not found at SAC/Cu interface in an isothermal annealed specimen. If the electron flux is changed to the reverse direction from Cu to SAC to Ni as for sample No.3, IMC at cathode Cu/SAC is binary Cu_6Sn_5 , Ni was not detected in the IMC. The Nickel atom diffusion driven by EM in this study is of interest as the existence of Ni atoms may affect the mechanical properties of IMC layer.

6.4.2 IMC Composition Effect on Elastic Modulus

The change of IMC composition will affect the elastic modulus and hardness of the IMCs and this is studied by nano-indentation tests. Nano-indentation was conducted on planar IMC surface. The solder joints were selective deep etched to remove the Sn

phase; the IMCs layer was exposed for investigation. As the IMCs at the interface tend to form a layer at the anode or cathode side during EM, it is convenient to measure the elastic modulus and hardness from planar surface. For tests on the planar surface, a test array 5*5 with a distance of 30 microns between two indentations measured. To confirm a test was performed on the IMC, and not on Cu or Ni layer, analysis of the load-displacement curve and modulus-displacement curve is needed. Indentation measurements were conducted on IMCs surface after completion of EM exposure for 10 days. Figure 6-14 shows the representative test curves for Cu_6Sn_5 at cathode Cu/SAC/electrolyticNi (electron flux from Cu to Ni), and NiCuSn at anode of Ni/SAC/Cu (electron flux from Cu to Ni). Figure 6-14(a) is the load-displacement curves. The corresponding elastic modulus and hardness, as a function of depth are shown in Figure 6-14(b-c). Considering the polished IMC layer thickness is only several microns. The average modulus and hardness is taken from low depth from 100 nm to 300nm. As shown in Figure 6-14(b), the value of modulus becomes “stable” after 50-100 nm, and it is independent of depth into surface.

Figure 6-14 Loads, modulus and hardness vs displacement curves for interfacial IMCs

(a. Load-displacement, b. Modulus-Displacement, c. hardness-displacement)

The elastic modulus for the samples 1 to 5 is given in Table 6-3. For the specimen No1, the exact composition was measure by electron probe micro analysis (EPMA). From the concentration of Cu, it can be seen that the Cu in IMC at anode is higher than that in cathode. The modulus of anode IMC for sample No.1 is 175 GPa, and is much higher than Cu_6Sn_5 , which is about 100 GPa. On cathode side it is mainly $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Cu}_4$, the modulus of it is 141GPa. For sample No.2, the formation of NiCuSn ternary IMC rather than Cu_6Sn_5 produce a high elastic modulus of 161 GPa. In contrast, the cathode IMC at sample No.3 is Cu_6Sn_5 , elastic modulus is 97.2 GPa, while the anode IMC is 176 GPa. The asymmetry of the mechanical properties again confirmed that the long distance atom diffusion behavior affected the composition change.

Previous work reported IMC growth and the change of modulus during isothermal aging [115]. The mechanical properties for binary IMC like Cu_6Sn_5 remain roughly constant with thermal aging. But for ternary IMC, like NiCuSn , the crystal structure and thus the mechanical properties are sensitive to the ratio of Ni and Cu content. More Ni will form $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Cu}_4$, while more Cu will form $(\text{Cu}_{1-x}\text{Ni}_x)_6\text{Sn}_5$. Vacancy or voiding in IMC may also affect the measurement. Due to the electromigration-induced atomic transport at the cathode side, voids will form and coalesce in the cathode IMC layer, thus the cathode IMC layer is not as dense as in anode. The measured elastic modulus becomes lower.

Table 6-3 Composition and elastic modulus of IMCs after EM exposure

No.	Solder joint	Cathode IMC/Modulus(GPa)	Anode IMC/ Modulus (GPa)
1	ENIG/SAC/ENIG	$*(\text{Ni}_{0.57}\text{Cu}_{0.43})_3\text{Cu}_4/141$	$*(\text{Cu}_{0.73}\text{Ni}_{0.27})_6\text{Sn}_5/175$
2	Electrolytic Ni/SAC/Cu	$\text{NiCuSn} / 138$	$\text{NiCuSn} / 161$
3	Cu/SAC/electrolytic Ni	$\text{Cu}_6\text{Sn}_5/ 97.2$	$\text{NiCuSn}/176$
4	Electrolytic Ni/SAC/ENIG	$\text{NiCuSn}/140$	$\text{NiCuSn}/160$
5	ENIG/SAC/electrolytic Ni	$\text{Ni, Cu, Sn(P)}/X$	NiCuSn/X

* measured by EPMA

6.5 EM-INDUCED BACK STRESS IN SOLDER

6.5.1 Movement of Indentation Marker

The in-situ observation of nano-indentation marker motion is shown Figure 6-15 where pictures were taken at 0h and 239h for comparison. The polished surface displays dark color and markers display as bright points. The markers displacements driven by electromigration at different locations were determined by measuring the distance from the marker center to the reference line behind copper pad using SEM pictures, is shown in Figure 6-16. As indicated in Figure 6-15, the electron flux and

atom flux were from top to bottom, experimental measurement showed that markers in the top 1, 2, 3 and 4th rows move upward during the electromigration exposure, which was as expected to be against the atom flux [127]. However, it was observed that the markers at the bottom rows moved downward. Some markers moved toward the anode and disappeared. As the marker motion was opposite to atom flux, this indicated that the atom flux near anode was upward. While for the row 5, the markers displacements were found to be much smaller than others. Figure 6-17(a) shows the displacement of the markers at different rows after 239 hrs vs. marker locations. There exists a “*neutral plane*” in which no net flux along either cathode or anode. The location of the “neutral plane” could be determined by the intersection of x axis and displacement curve. The distance from the neutral plane to the anode interface is about 55 μm .

Figure 6-15 Marker displacement observed by CCD microscope (a) 0h and (b) 239h.

Figure 6-16 Marker movement measurement

Figure 6-17 Marker motion and stress gradient (a) Marker displacement after 239 hrs, (b) stress gradient

6.5.2 Back Stress and Stress Gradient

In analyzing the atom flux in the solder joint, electron wind force and the back stress were considered to affect the motion of Sn atom [127],

$$J_{em} = -C \frac{D}{kT} \frac{d\sigma\Omega}{dx} + C \frac{D}{kT} Z^* eE \quad (6-2)$$

where J_{em} is atom flux in unit of atoms/cm²s, C the concentration of atoms per unit volume, D/kT atom mobility, σ the hydrostatic stress in the metal and $d\sigma/dx$ the stress gradient along the direction of electron flux, Ω atom volume, Z^* effective charge number of electromigration, e the electron charge, E the electric field and $E=\rho j$, ρ is the electrical resistivity, j the current density. The value of atom flux of electromigration, J_{em} can be estimated by the motion of embedded particles [133],

$$J_{em} = \frac{V_{EM}}{\Omega A t} = \frac{u}{\Omega t} \quad (6-3)$$

where V_{EM} is the volume of solder moved by electromigration, which was calculated as the marker displacement multiplied by the cross-sectional solder area A . u

is the marker displacement, t is the electromigration time. Combining Eqn 6-2 and Eqn 6-3 gives

$$\frac{d\sigma}{dx} - \frac{Z^* e \rho j}{\Omega} = -\frac{1}{C} \frac{kT}{D} \frac{u}{\Omega^2 t} \quad (6-4)$$

let $K = \frac{1}{C} \frac{kT}{D} \frac{1}{\Omega^2 t}$, where K is a constant as temperature and time are given. We

assume that the back stress on the marker displacement near to cathode could be neglected, or the stress gradient $d\sigma/dx = 0$. The marker displacement near cathode $u_0 = 11.3 \mu m$. Thus at cathode only the second term remains at the left in Eqn 6-4,

$$\frac{Z^* e \rho j}{\Omega} = K * u_0 \quad (6-5)$$

At the neutral plane, the marker displacement $u=0$, from Eqn 6-5,

$$\frac{d\sigma}{dx} - \frac{Z^* e \rho j}{\Omega} = 0 \quad (6-6)$$

it is assumed that EM stress gradient is roughly constant in the solder bump, thus at the neutral plane,

$$\frac{d\sigma}{dx} = \frac{Z^* e \rho j}{\Omega} = K * u_0 \quad (6-7)$$

For markers at any other location, the marker displacement u (unit, μm), which was experimentally determined as shown in Figure 6-17(a), could be expressed as function of $u(x)$ using a curve fitted polynomial,

$$u(x) = 11.3 - 0.026x + 4 \times 10^{-4} x^2 - 2 \times 10^{-6} x^3 \quad (6-8)$$

and

$$\frac{d\sigma}{dx} - \frac{Z^* e \rho j}{\Omega} = -K * u \quad (6-9)$$

substitute (6-5) into (6-9), the stress gradient as a function of marker displacement,

$$\frac{d\sigma}{dx} = K(u_0 - u) \quad (6-10)$$

thus the stress at any location as integration of stress gradient,

$$\sigma = \int_0^x K(u_0 - u)dx \quad (6-11)$$

at the anode interface, the maximum stress is the yield stress of SnAgCu alloy (20MPa for 125C). Since the hillocks were already observed in the anode side, we can anticipated that the yield stress was achieved at anode interface,

$$\sigma_y = \int_0^{x_a} K(u_0 - u)dx \quad (6-12)$$

by substituting Eqn 6-8 into Eqn 6-12 and assuming the boundary stress 20MPa, the constant K could be determined as $6.93 \times 10^{15} \text{N/m}^4$. Thus, by substituting K into Eqn 6-11 and Eqn 6-12, the stress and stress gradient at any place could be determined, respectively. As given in Table 6-4. At the neutral plane, the stress gradient is 97kPa/ μm and stress is 9.01MPa.

Table 6-4 Calculated back stress, stress gradient and Z^*

Factors	Value/expression	Neutral plane
Stress gradient	$\frac{d\sigma}{dx} = K(u_0 - u)$	$\frac{d\sigma}{dx} = 97 \text{ kPa} / \mu\text{m}$
Stress	$\sigma = \int_0^x K(u_0 - u)dx$	$\sigma = 9.01 \text{ MPa}$
K	$6.93 \times 10^{15} \text{ N/m}^4$	
Z^*	1.5	Eqn 6-13

Figure 6-17(b) shows the stress gradient as a function of distance to cathode, where the constant EM stress gradient is also plotted. The driving force of atom flux is combination of these two mechanisms. From Eqn 6-6, the effective charge number Z^* could be determined as,

$$Z^* = \frac{\Omega}{e\rho j} \left[\frac{d\sigma}{dx} \right]_{\text{Neutral}} \quad (6-13)$$

where $\Omega_{\text{Sn}} = 2.71 \times 10^{-29} \text{ m}^3$, $e = 1.6 \times 10^{-19} \text{ C}$, $\rho_{\text{Sn}} = 1.09 \times 10^{-7} \text{ Ohm} \cdot \text{m}$, $j = 1 \times 10^4 \text{ A/cm}^2$,

thus Z^* is determined as about 1.5. This is close to the value reported by Hu and Huntington (1.8) [134], but much smaller than reported values (7 for pure tin and 50 for Sn in eutectic SnPb) by Liu et al [135]. However, the measurement in this study by nano-indentation marker is different Ref. [135] as the activation energy is not a factor needed to determine Z^* .

6.5.3 Reverse Marks Motion

The observed reverse markers motion near the anode indicates a net reverse atom flux from the anode to the cathode. From the Eqn 6-4 analysis, this would lead to an ambiguous conclusion that the back stress gradient is even larger than EM stress gradient near anode. However, the current distribution near anode is far from uniform due to the geometry and surface effect. The reverse atom flux due to back stress tends to occur in the low current density region which is near the surface. It does not mean the back-stress is larger than the EM. In eutectic SnPb solder joint, a back flow of Sn under EM respect to Pb was observed as well [133]. At the anode, where the current gets out is where the atoms build-up and has the highest compressive stress, the atoms inside will diffuse to the solder surface to form hillocks or go back to the solder along the back stress gradient. So at surface it has a big effect on the reverse motion of markers. The markers in high stress region are deformed. The reverse atom movement is eliminated at the neutral plane by electromigration atom flux. These atoms finally form hillock between the anode and the neutral plane. The neutral plane underneath the surface may be closer to anode, or the anode itself.

Blech observed the reverse atom motion at the anode due to stress relaxation after the removal of electromigration driving force [130]. With in-situ measurement, it was confirmed that the reverse marker motion in our study is not due to stress relaxation. It took 239 hrs for the markers (near to anode) to move about 10 μm toward anode. Stress

relaxation effect on marker motion is not detectable by comparing the images before and after turn-off the applied current.

6.6 MORPHOLOGY CHANGE OF INDENTATION MARKERS

The change of the marker morphology was characterized under SEM. Figure 6-18(a-c) shows the change of small markers subject to time. It can be seen from Figure 6-18(b) and (c) that, the shape of the triangle indentation marker is damaged due the electromigration. Void grows from the edge of the indentation marker against the direction of the electron flow, while Sn atoms pile up at the other side.

Figure 6-18 Damage of small marker during EM exposure (a) 0h, (b) 120h and (c) 240h

The change of large markers subject to time for the indentation depth of 3 μm is shown in Figure 6-19(a-c). The behaviors of indentation mark with depths of 3 μm and 8 μm are similar. In contrast with small marker change shown in Figure 6-18, large markers can maintain their shape during the EM exposure. As shown in Figure 6-19 (b) and (c), the sizes of the markers are 20 μm in width, which is 2-3 times larger than the

Sn rich grains. Sn atoms pile up at the bottom of the marker, while at the top side; depletion of atoms could be seen. Considering the surface diffusion on the indentation marker surface, electromigration will drive atoms on the top surface of the void to the bottom surface of the void, this would caused the depletion of atoms at top side and hillocks or piling up at the bottom of the marker.

Figure 6-19 changes in large marker fractures during electromigration exposure (a) 0h, (b) 120h and (c) 240h

Pre-existed voids often presents in the solder joint, which form during the soldering reflow. The indentation marker on the surface can be deemed as pre-existed void. From the change of the marker morphology and marker movement, it is anticipated that the pre-existed void show the similar behavior. Since the current in the void is zero, while the density near the void is several times higher than average, electromigration can lead to redistribution of current and thus stress graident develop around the void.

6.7 SUMMARY

In summary, EM has significant impact on IMC layer growth, both in growth rate and composition. IMC layer growth at anode interface is faster than cathode interface. Elastic modulus and hardness were measured by nano-indentation at the interfacial IMCs after EM exposure and vary on anode and cathode sides. Elastic modulus for the IMC at anode SAC/Ni side is higher at 180-190 GPa, while the value at cathode Ni/SAC side is lower at 130-140 GPa. EDX Line Scan Analysis from cathode to anode and EPMA measurement confirmed the long range Ni diffusion driven by EM. This affected composition of the IMC and the change corresponds in mechanical properties. Voids will form and coalesce in the cathode IMC layer, thus the cathode IMC layer is not as dense as in anode. The measured elastic modulus can also become lower. The distribution of back stress, stress gradient and effective charge number Z^* were determined by measuring area array nano-indentation marker motion. The indentation marker on the surface can be deemed as pre-existed void, which has significant effect on electromigration.

CHAPTER 7 DROP IMPACT FAILURE AND ANALYSIS

The effect of thermal cycling aging on board level drop reliability for lead-free SnAgCu (SAC) in fine pitch ball grid array (FPBGA) packages is studied in this chapter. The drop life was observed before and after thermal cycling aging. Comparison of SAC/ENIG packages to SAC/OSP packages was investigated.

7.1 BACKGROUND

In accelerated thermal cycling (ATC) tests, the cyclic excursions of temperatures between -40°C to $+125^{\circ}\text{C}$ cause concurrent degradation of the solder joints and result in IMC growth [136] and thermal fatigue damage. The IMC growth, as well as the void/crack formation subject to isothermal aging and thermal cycling aging is expected to affect the long-term solder joint reliability performance. It can also affect the impact shock reliability as thicker IMC layer cause brittle fracture failure. The growing use of portable electronics devices such as cell phone and PDA has led to increased concerns on drop impact related failures in electronic assemblies. The studies on impact drop test on lead-free solder joint reliability have been reported [137-142]. Brittle fracture of IMC caused by dynamic loading such as impact shock is the dominant failure mode [142]. During service of electronic products, the solder joint is exposed to thermal aging before accidental drop impact occurs. The solder joints are subjected to thermo-mechanical induced stress-strains leading to solder fatigue degradation. Board level drop impact test and finite elements modeling have been reported [142-144]. The effect of IMC growth and presence of Kirkendall void formation subject to thermal aging has been reported [145-147]. For the portable electronic products, it is necessary to test the drop impact reliability after a period of usage.

The effect of thermal cycling aging on drop impact reliability has been investigated. A 15x15mm fine-pitch BGA (FPBGA) with 324 I/O was subject to drop test. Lead-free SAC with either organic solderability preservative (OSP) or electroless nickel immersion gold (ENIG) surface finishes was used. Interfacial IMCs, Kirkendall voids formation and interconnect failure mode are studied subject to TC aging. Kirkendall voids were observed with Ar⁺ sputtering etching. The failure sites and mechanism were then examined and correlated with IMC and void formation.

7.2 EXPERIMENTAL PROCEDURES

7.2.1 Test Setup and Measurement

The Lansmont test machine was used to provide the drop impact load for board-level FPBGA soldered assemblies. A half sine g-input shock pulse on the drop table is calibrated to drop height and the felt pads on drop base to give the required g-input pulse and time duration. The drop machine structure consists of a steel base, two solid chrome plated guide rods, drop table and hoist positioning system as shown in Figure 7-1. The aluminum welded table has an assembled mass of 190.5kg.

Table 7-1 FPBGA specimen and thermal aging condition

Solder Joint	Aging Temperature	Aging Time
SAC/Cu-OSP	-40 ~ 125 °C (TC)	500, 1000, 1500 TCs
SAC/ENIG	-40 ~ 125 °C (TC)	500, 1000, 1500 TCs
SAC/Cu-OSP	125, 150 °C	0,120,240,360 hrs
SAC/ENIG	125, 150 °C	0,120,240,360 hrs

Figure 7-1 Drop impact test vehicle and setup

The experiment matrix and sample aging condition are given in Table 7-1. The test specimen with seven mounted FPBGA (324 I/O) units soldered onto the printed circuit board are shown in Figure 7-2. The test board (1 mm thick) either has organic solderability preservative (OSP) on copper pads (Cu-OSP) or electroless nickel and immersion gold (ENIG, or NiAu) surface finish. The FPBGA package is daisy chained, with full interconnection failure monitoring of the solder joint. Multiple fault isolation pads are designed-in for the purpose of easy identification of failure distribution.

Figure 7-2 PCB test board (77x132mm) with 15x15mm FPBGA Packages

Thermal cycling (TC) aging was conducted with TC profile of -40°C to $+125^{\circ}\text{C}$. The cycle time was 1 hr, where 15 minutes at upper soak and lower soak temperature, respectively. Isothermal aging at 125 and 150°C was also conducted for comparison. After 0, 500, 1000 and 1500 cycles, the test boards were taken out from

TC chamber for board level drop impact tests. The test board was screw-mounted to the drop table at 4 corners with the units facing downwards.

Figure 7-3 Drop Test Fixture with PCB Mounted onto it

The drop height was set at 1.0m with the impact base surface covered with felt pad. The drop orientation is in the horizontal plane with packages in a face-down position. The test PCB was screwed onto the drop table at four support pin locations (see Figure 7-3). During the test, the drop table is raised and dropped from the desired height (1m). Upon impact, the drop responses of interest is the shock g-level (G-input) experienced by the drop table and the PCB (G-output) and the bending strain experienced at the center the PCB. The static and dynamic resistances of the daisy-chained solder joints were recorded. The peak G-input shock pulse of the drop table was about 690g in the form of a half-sine wave with a 2 millisecond period. An accelerometer was mounted on the drop table near to the fixture to measure the input acceleration (G-input). For drop test consistency and repeatability, drop responses of input/output acceleration and PCB strain were monitored.

7.2.2 Dynamic Response and Failure Detection

The dynamic measurement method used for monitoring resistance of daisy-chained solder assembly in real-time during drop impact is shown in Figure 7-4. A constant resistor, R_0 , is placed in series with the daisy chain resistance of R_x , and connected to a DC power supply. The oscilloscope was used to measure the dynamic voltage drop on daisy chain loop. The dynamic resistance of solder joints, R_x , can be expressed as:

$$R_x = \frac{R_0 V_x}{U - V_x} \quad (7-1)$$

where U is the voltage of the DC power supply and 1.8volts was used in this test, V_x is the dynamic voltage of daisy chain measured by oscilloscope, R_0 is the constant resistance of 10Ω used in this test. When $V_x \rightarrow U$, $R_x \rightarrow \infty$ (implies an open circuit), it indicates the critical solder joint has failed. Three solder joint daisy-chained current loops for components labeled “A”, “B”, and “C” as shown in Figure 7-4 were monitored by three oscilloscope channels for one test board.

Figure 7-4 Dynamic resistance measurement setup

In a drop test, it is common to observe that the solder joint crack opens up resulting in a resistance discontinuity and closes back to resume electrical continuity. The upward/downward deflection of the PCB leads to the opening/closing mode of the crack, which is known as an intermittent solder joint failure. When the crack becomes larger and cannot close back after the impact test, a permanent solder joint failure is recorded. In this study, the permanent solder joint failure is identified as the failure criteria.

7.2.3 Failure Characterization

After TC aging and drop test, the specimens were cross-sectioned and observed by Scanning Electron Microscopy (SEM) under an accelerated voltage 15kV and backscattered electron mode (BSE). The IMC layer at the interface was examined at high resolution. Characterization of IMC thickness and Kirkendall voids after thermal cycling was conducted. The specimen was cross-sectioned and polished, and then it was etched by Ar⁺ sputtering with a R.F. magnetron sputtering equipment. After the chamber was evacuated to 10⁻⁶ Pa, argon was introduced to maintain working pressure. The specimens were etched by Ar⁺ for 10 min with a power of 120W.

7.3 BOARD LEVEL DROP CHARACTERIZATION

7.3.1 Drop Impact Lifetime Comparison before and after TC Aging

The resistance of daisy-chained solder joints was monitored during thermal aging. The drop lifetime was monitored by the change of dynamic resistance for the daisy-chained solder joints in real-time during drop impact. During drop test, the solder joints resistance (or “voltage”) for the FPBGA packages and PCB bending strain were captured. A typical response is showed in Figure 7-5. It can be divided into two regions, before impact (static) and after impact (dynamic). Test result for as reflowed

board after a certain number of drops is used for illustration. Channel 1 is used for dynamic strain measurement at the PCB center upon impact. Channels 2, 3 and 4 are measuring the dynamic voltages of package units 1, 8 and 15 respectively. Before impact, the PCB strain is zero while the static solder joint resistance is similar to the value measured by manual probing. Each package location has its own zero-reference voltage and initial voltage reading as indicated. With reference to channel 3 (unit 8), a peak voltage was registered after impact, indicating that an initial failure in a solder joint has occurred. The following fluctuation in peaks constituted with the upward/downward flexing of the PCB and shows the opening/closing mode of the cracking behavior. When flexing of the board has ended, static resistance measurement by manual probing was not able to register any discontinuity. This observation describes the intermittent solder joint failure. At subsequent drops, unit 8 would register fluctuation in voltage reading and finally the discontinuity was confirmed by manually probing with an open circuit being measured, thus implying that the solder joint has opened permanent.

Figure 7-5 Typical Dynamic Responses for Drop Test

The drop test was conducted until all the units on the board had failed. The average number of drop cycles to initial failure after each thermal condition was recorded as the drop impact lifetime. Average drop impact lifetime vs. thermal aging for SAC/Cu-OSP and SAC/ENIG were plotted in Figure 7-6(a-b).

(a) SAC/Cu-OSP

(b) SAC/ENIG

Figure 7-6 Board level drop lifetime before and after thermal cycling aging

For the FPBGA assembly on board, the units are classified to three groups due to their location and symmetry of the board: (1) Edge units C3 and C13, which has the

shortest lifetime; (2) Center units C8 and; (3) Corner units C1, C5, C11 and C15. It can be seen from Figure 7-6 that the drop lifetime decreased significantly after thermal aging conditioning followed by drop test. For all the units in this study, drop lifetime could decrease by more than 50% only after 500 cycles of TC aging or 120 hrs isothermal aging. This is even more significant after longer thermal aging time. For SAC/Cu-OSP after 1000 and 1500 cycles of TC, or after isothermal aging of 240 and 390 hrs, the drop impact lifetime reduced down to 5 drops or even worse.

Figure 7-7 Drop lifetime for unit C3 and C13 before and after TC aging

For as reflowed specimens, take unit C3 and C13 as examples, as shown in Figure 7-7. The drop lifetime for SAC/Cu-OSP (29 drops) is better than SAC/ENIG (21 drops). This is reasonable as needle-like IMC (SAC/ENIG) is not as resistant to IMC fracture as scallop IMC layer (SAC/Cu-OSP). The failure crack morphology is characterized in the following sections. For the drop lifetime performance of different surface finish, however, SAC/ENIG seems to be better than SAC/Cu-OSP after thermal cycling aging. The drop impact lifetime significantly decreased from 29 to 6 for SAC/Cu-OSP, after only 500 TC aging. After 1000 and 1500 cycles of TC aging, the specimen can only

endure 1 drop before failure occur. The drop lifetimes for SAC/ENIG after 500, 1000 and 1500 were 13, 9 and 8, respectively and were obviously better than SAC/Cu-OSP.

7.3.2 Characterization of Failure Modes

The drop impact failure was characterized from both plane-view and cross-section observation. For plan-view observation, dye penetration was used to mark the failure site. Blue ink 35vol% + ethanol 65% was used as a dye penetration solution. The FPBGA unit was then pilled off from the board, the marked failure site display purple-blue color under optical microscope. Among the 324 BGA I/Os in one unit, the typical drop impact failure occurred at the corner or edge of the unit. The solder joints failure distribution across the PCB is, however, location dependant. Due to pure bending mode in location (2) or C8, joints at corner of the package failed as a result. Damage by shock wave transmission through the support pins was evidently demonstrated for units in group (3), where joints at the package corner had failed. For group I, failure was registered at left and right rows of the package. The failure location mapping was preformed after all units in a single board had failed. Thus it may have failed to capture the first solder joint crack occurring at the corner of the package. The subsequent drop cycles resulted in adjacent joints to fail. The failure distribution was similar for all test specimens.

For all of the tested boards with the two different PCB surface finish (Cu-OSP and ENIG) and thermal aging profiles, it showed that the drop impact failure occurred at multiple locations. Four types of possible solder joint failure were detected after drop impact as shown in Figure 7-8. They are; (1) IMC failure between SAC/Cu pad at the PCB side, as shown in Figure 7-8(a), solder joint detached from the pad through the IMC interface. The IMC failure is the dominant failure mode in this study. (2)

Pad/substrate failure at the PCB side, as shown in Figure 7-8(b), the copper pad totally detached from the resin substrate, the fibers in PCB could be clearly seen in plane-view. (3) IMC/solder failure at the component side, as shown in Figure 7-8(c), in which the solder ball was left at the board side, the crack could be either in the IMC or in solder near the interface. (4) Copper trace failure, as shown in Figure 7-8(d), it can be seen that copper trace broken must be accompany with the Pad/substrate open. When the copper pad is detached from substrate, the dog-bone shape copper trace would be easily broken at the route of the one end.

The solder joint failure mode subject to TC aging was reported [148-150]. The typical fatigue failure after TC aging occurred in the SAC solder near the component interface, as shown in Figure 7-9(a), the location of solder joint failure was typically at the outmost component corner or die corner. After 500 to 1500 cycles of TC aging, the crack in solder joint is expected to propagate already, which could affect the drop reliability significantly. However, the failure site after drop impact test was not where the thermal fatigue crack initiated. The dominant failure is still the brittle failure of IMC, at IMC layer on the SAC/Cu pad at board side, as shown in Figure 7-9(b). The solder ball was totally separated from the copper pad.

(a) IMC failure between SAC/Cu pad at the PCB side

(b) Pad/resin failure at the PCB side

(c) IMC/solder failure at the component side

(d) Copper trace failure

Figure 7-8 Solder joint failure modes subject to drop impact

Figure 7-9 Solder joint failure subject to (a) TC, failure in SAC solder near component interface, (b) Drop impact, failure in IMC at PCB side

7.4 IMC FAILURE ANALYSIS

7.4.1 Drop Impact Crack Propagation

In this section, the first type of drop impact failure, IMC failure between SAC/Cu pads were observed under high resolution SEM (BSE mode) for SAC/Cu-OSP and SAC/ENIG test board. The drop tests were conducted after different TC aging time. Figure 7-10(a-d) show the enlarged drop impact failure interface for the SAC/Cu-OSP specimens with 0, 500 1000 or 1500 TC aging. Although all the four failure occurred in the IMC, the location of the crack path is different. For as reflowed specimen shown in Figure 7-10(a), the crack path is random in the Cu_6Sn_5 IMC, either near the Cu- Cu_6Sn_5 interface, or near the SAC- Cu_6Sn_5 interface, or in the middle of Cu_6Sn_5 . For the specimen after 500 TCs as shown in Figure 7-10(b), a dominant crack can be seen in the Cu_6Sn_5 IMC, while quite a lot inclined tiny cracks exist. These tiny cracks stopped at the interface of IMC and copper pad. After 1000 TC aging, the crack became very close to the IMC/copper interface, where the Cu_3Sn grow during TC aging. The crack is flatter compared to the as-reflowed condition and 500 cycles TC aging specimens. This is even more significant for the specimen after 1500 cycles of

TC aging, as shown in Figure 7-10(c); the crack propagates merely through the bottom Cu-IMC interface.

Figure 7-10 SAC Solder to Copper pad interface after drop impact test for (a) as-reflowed, (b) 500 TC, (c) 1000 TC and (d) 1500 TC.

The drop impact failure interface for the SAC/ENIG specimens after 0, 500 1000 or 1500 cycles of TC aging is given in Figure 7-11 (a-d). For as reflowed specimen shown in Figure 7-11(a), the crack occurred at the interface between IMC and Ni(P) layer. This is different from SAC/Cu-OSP which has scallop IMC layer. The ternary needle-like NiCuSn IMC did not form a compact layer at the interface. After 500 TCs, the dominant crack was again at the IMC/Ni(P) interface. It is noted that vertical crack features penetrates the Ni(P) layer and stopped at the interface of Ni(P) and copper pad. This indicates that the Ni(P) layer exhibit brittle fracture weakness. After 1000 cycles of TC aging, the Ni(P) layer was further consumed and the crack was at the IMC/Ni(P) interface. The Ni(P) layer became very thin at some locations, and

voids can be seen as shown in Figure 7-11(c). During thermal cycling aging, NiCuSn ternary IMC grow in thickness but it may not be in planner-like. Spalling of IMC could be seen, as shown in Figure 7-11(d) after 1500 cycles of TC aging. The Ni(P) layer degraded, as the crack form at the interface of Ni(P) and Copper pad. The interface microstructure requires further characterization for both SAC/Cu-OSP and SAC/ENIG after TC aging to examine why the crack paths change and how the IMC growth affects the solder joint strength.

Figure 7-11 SAC Solder to ENIG interface after drop impact test for (a) as-reflowed, (b) TC 500, (c) TC 1000 and (d) TC 1500.

7.4.2. Kirkendall Voids Characterization

During TC aging, solid state Cu-Sn interdiffusion process continues to grow the IMC layer. Earlier studies [147-150] reported the formation of Kirkendall voids in the Cu-Cu₃Sn interface and Cu₃Sn compound layer when the SAC/Cu solder joints were subject to isothermal aging. For the two elements, Cu was the dominant diffusing

species through Cu_3Sn and Cu_6Sn_5 . In the Cu-SAC solder reaction couple, the diffusing Cu atoms arrive at Cu_3Sn - Cu_6Sn_5 and Cu_6Sn_5 -solder interfaces and result in the growth of both IMC layers. Because of the unbalanced Cu-Sn interdiffusion through interface, atomic-level vacancies left by the migrating Cu atoms on the bare Cu side are not filled by Sn atoms. These vacancies coalesce into the so-called Kirkendall voids.

However, the voids were so small that they would be smeared with the normal mechanical polishing process and cannot be seen in typical SEM pictures. The SEM pictures reported by Chiu and Zeng [146] were taken from samples cross-sectioned by FIB (Focused Ion Beam). In this study, Ar^+ ion sputtering was used to reveal the tiny Kirkendall voids. The formation and growth of the Kirkendall voids at the Cu-solder interface after TC aging are shown in Figure 7-12.

Figure 7-12 SAC solder to copper pad interface after Ar^+ sputtering etch (a) as reflowed specimen, (b) TC 500 Kirkendall voids formed and occupied about 10% of

the interface and (c)TC 1000, growth of Kirkendall voids is noted, micro-crack could be seen at the interface

For as reflowed specimen shown in Figure 7-12(a), no voids could be seen at the interface. While after 500 TCs, it can be seen that many Kirkendall voids formed at the Cu-IMC interface, where Cu_3Sn is located. It occupied about 20% of the interface length, shown in Figure 7-12(b). The density of the voids area further increases as the thermal aging increased to 1000 cycles of aging. As shown in Figure 7-12(c), the voids coalesced and generated micro-cracks at the interface. This voiding process seems to develop faster than the case isothermal aging at 125 °C reported by Chiu [146]. Dynamic recrystallization at the Solder/ Cu_6Sn_5 interface could accelerate the interdiffusion of Cu atoms. The unbalanced Cu-Sn interdiffusion through the interface is significant, and Kirkendall voiding process under TC aging is more serious than isothermal aging.

The growth of Kirkendall voids explain why the TC aging effect on drop impact durability reduced significantly for SAC/Cu-OSP soldered assemblies. At the sub-micron level, the voids form near the Cu/IMC interface and coalesce during TC aging. Cracks propagate more readily at the interface than in the IMC layer. Thus the morphology of the crack path becomes flatter after TC aging, and the drop impact lifetime decreased significantly.

The SAC/Ni(P) interfacial microstructure after TC aging were observed by SEM BSE mode after Ar^+ sputtering. Figure 7-13(a-c) showed the images for TC aging after 500, 1000 and 1500 cycles, respectively. Voids were found in the Ni(P) layer after 500 cycles of TC aging. These voids had rod shape and were perpendicular to the Ni(P) layer, or called vertical void in contrast to the horizontal voids which is parallel to the

Ni(P) layer. This is consistent with the observation shown in Figure 7-13(b,c), where quite a lot vertical crack were found in Ni(P) layer. After 1000 cycles of TC aging, the Ni layer became thinner and there were more vertical voids formed. After 1500 cycles of TC aging, layered horizontal void formed at the interface of Cu/Ni(P). Compared with crack propagation shown in Figure 7-13(d), it is clear that these horizontal voids degraded the Ni/Cu layer joint strength. From the above characterization of interfacial void after Ar⁺ sputtering, we can see the effect of TC on the interfacial voiding process and subsequently drop impact lifetime. Although both BGA units with SAC/Cu-OSP and SAC/ENIG solder joint showed good drop impact reliability before TC aging, their performance after TC are not acceptable.

Figure 7-13 SAC solder to ENIG interface after Ar⁺ sputtering etch (a) TC 500, (b) TC 1000 vertical voids could be seen in Ni(P) layer, and (c) TC 1500, horizontal void developed at Ni(P)/Cu interface

7.5 SUMMARY

Thermal cycling aging shows significant effect on board level drop reliability for SAC soldered FPBGA packages in this study. SAC/ENIG packages exhibits longer drop impact life after thermal aging than that of SAC/OSP. Kirkendall voids formation and solder joint failure mode are characterized by SEM after Ar⁺ sputtering. It was found that growth of Kirkendall voids and IMC significantly weakened the solder joint interface with TC aging. Drop impact crack path locations changed from the IMC to the IMC/Cu interface. For SAC/ENIG specimen, vertical and horizontal void in Ni(P) layer was found after TC aging, drop impact crack propagates between Ni(P)/Cu pad interface along the horizontal voids.

CHAPTER 8 CONCLUSIONS

8.1 CONCLUSIONS

Interconnection failures in lead-free soldered assemblies subject to thermal, mechanical and electrical loadings have been studied. The IMC growth between 95.5Sn-3.8Ag-0.7Cu lead-free solder and Cu pad or ENIG surface finish subject to isothermal and thermal cycling aging were investigated. An integrated IMC growth model for thermal cycling aging as a function of temperature and time is proposed. The mechanical properties of IMCs and solder alloy before and after thermal aging were characterized by nano-indentation. A new approach of deriving strain-rate dependant properties for elastic modulus and hardness of solder was characterized for the strain rates of 10^{-3} to 10 (1/s). Electromigration effect on IMC growth and elastic modulus measurements by nano-indentation were compared at cathode side and anode side of solder joint. Electromigration-induced back stress and stress gradient were analyzed by studying the motion of an array of nano-indentation markers subject to current stressing. The effect of thermal aging on Kirkendall void formation and the subsequent effect of Kirkendall voids on board level drop impact failure were characterized in details. Based on the analyses carried out in the previous chapters, the following specific conclusions can be drawn accordingly:

8.1.1 SAC Solder Joint Microstructure and IMC

The IMC in solder matrix, Ag_3Sn and Cu_6Sn_5 , were characterized in detail and the formation of needle-like or rod-like features are several microns in size. Large plate-like Ag_3Sn and hexagonal hollow-centered Cu_6Sn_5 intermetallic tubes characterized after different durations of soldering reflow time. Large Ag_3Sn plates were often connected to the metallization interface. The IMC thickness as a function of reflow

time was determined for both SAC/Cu and SAC/Ni couple system. For solder/Cu, the morphologies of the Cu_6Sn_5 are typically scallop-like over reflow time. The size of Cu_6Sn_5 IMC increases rapidly. The growth rate of NiCuSn intermetallic is much lower compared to Cu-Sn IMC. The morphology changes dramatically subject to reflow time.

8.1.2 Thermal Aging Effect on IMC Growth

The IMC growth kinetic for lead-free solder interface subject to isothermal (100, 125 and 150 °C) and thermal cycling aging (-40 to 125 °C) are compared for different solder/substrate interfaces. A time-integrated IMC growth model has been developed to predict the IMC growth for typical thermal cycling aging profiles. It is noted that the major contribution of IMC growth during thermal shock (TS) and thermal cycling (TC) aging is from the high soak and dwell temperature at 125°C. An acceleration factor, K , is proposed to calibrate the thermal stress-strain effect on IMC growth subject to TC and TS compared to isothermal aging IMC growth. Thermal fatigue failure for PBGA assemblies subjected to thermal cycling aging was investigated. Digital image speckle analysis (DISA) shows that strain concentrates at the corner of the solder joint, where thermal fatigue crack initiate and propagate. The IMC growth rate subject to thermal cycling was found to vary for the solder joints at various locations in the PBGA assembly. The highest IMC layer thickness was observed at the outermost solder joint. Thermal stress-strains are generated by CTE mismatch during temperature cycling loading and can affect the IMC growth rate.

8.1.3 Nanoindentation Analysis

The apparent elastic modulus and hardness for SAC387 solder alloy, IMC layer at the pad substrate were determined for the condition before and after thermal aging by nanoindentation. A planar IMC surface nano-indentation approach was proposed for comparison to reported work on nano-indentation tests on cross-sectioned specimens.

Elastic modulus of the NiCuSn IMC at SAC/ENIG specimen changed from initially 207 GPa to 146 GPa with aging time up to 500 hrs at 125 °C, The hardness decreased from 10.0 GPa to 7.3 GPa correspondingly. For SAC/Cu-OSP reaction couple, elastic modulus of Cu₆Sn₅ remains constant at 97.0 GPa and hardness at 5.7 GPa. The crystal structure of NiCuSn ternary IMC changed from (Cu_{1-x}Ni_x)₆Sn₅ to (Ni_{1-x}Cu_x)₃Sn₄. The creep effect on the measured result was analyzed when testing SSAC solder. It was found that the indentation penetration, and thus the hardness, is loading rate dependent. The indentation strain-rate dependant properties for hardness and elastic modulus were measured from strain rates of 0.001 to 10 (s⁻¹). The value of the hardness changed from 130 MPa to 520 MPa with increase in strain rate due to dynamic hardening effects.

8.1.4 Electromigration Effect on IMC Growth and Back Stress in Solder Joint

The impact of Electromigration (EM) on isothermal aging IMC growth in Ni/SAC/Ni, Cu/SAC/Ni single BGA solder joint and FPBGA soldered assembly at anode side and cathode side were investigated. The solder joints were subjected to a current density of 5000 A/cm² and isothermal aging condition at 150°C. This is to study the effects of combining thermal diffusion and electromigration. IMC growth at anode side is faster than at the cathode interface. Both IMC growths are faster than pure isothermal aging at 150 °C due to the joule heating effect which can raise the solder temperature to 170 °C. The composition of IMC, the elastic modulus and hardness properties were determined after EM exposure up to 10 days at 5000A/cm². The elastic modulus for the IMC at anode (SAC/ENIG) side is around 180-190 GPa, while at cathode (ENIG/SAC) side it is between 130-140 GPa. EDX line scan analysis from cathode to anode shows the presence and transport of Ni species at the anode IMC of SAC/Cu in Ni/SAC/Cu joint. EPMA measurements on Ni/SAC/Ni specimen also confirmed the long range Ni and Cu atom diffusion transport driven by EM flow effects

causing the composition of the IMC to change and its mechanical properties to change as well.

EM induced back stress on atom transport motion were studied using an array of nanoindentation markers on cross-sectioned FPBGA specimens. The marker motions driven by a combination of electrical and induced back stress effects were measured at different location. The distribution of back stress, stress gradient and effective charge number Z^* were determined. Most of the indentation markers move towards the cathode, which is against the atomic flux. However, reverse marker movement was detected near the anode interface caused by the back stress gradient where a reverse flux of Sn atom from the anode to cathode is generated. The neutral plane, where back stress gradient and EM stress gradient is in equilibrium, was experimentally determined. The stress and stress gradient at the neutral plane were measured as 9.0 MPa and 97 kPa/ μm , respectively. Nano-indentation marker was used as dummy voids to study the effect of pre-existed void or defects on EM degradation.

8.1.5 Board Level Drop Failure and Analysis

The effect of thermal cycling aging on board level drop reliability for SAC solder joints was studied in detail. Drop impact tests conducted after thermal cycling aging or isothermal aging show a transition of failure modes and significant reduction in drop durability of solder joint. Significant decrease in drop life was observed for both SAC/ENIG and SAC/Cu-OSP soldered assemblies. SAC/ENIG solder joints exhibits better drop impact reliability after thermal aging than compared to SAC/Cu-OSP solder joints. The IMC growth, Kirkendall voids formation and solder joint failure mode are characterized by SEM after Ar^+ sputtering. It was found that the growth of Kirkendall voids and IMC layer significantly weakened the solder joint interface during TC aging. Drop impact fracture crack path location changed from the IMC layer to the IMC/Cu-

pad interface, and is related to Kirkendall void formation location. For SAC/ENIG specimen, vertical and horizontal void in Ni(P) layer were found after TC aging. Drop impact crack path propagates between Ni(P)/Cu pad interface along the horizontal void location.

8.2 ACHIEVEMENTS AND RECOMMENDATIONS

8.2.1 Achievements

The major achievements and new contributions of this PhD project are as follows:

1. A temperature and time integrated IMC growth model has been proposed for the first time to predict the IMC growth behavior subject to thermal cycling aging. The IMC growth kinetic for SAC solder interface subject to thermal cycling aging was characterized for solder/substrate interface with Cu or ENIG surface finish. Comparative study of IMC layer thickness growth by isothermal aging (at 125 °C) versus thermal cycling aging (-40 to +125 °C) provides the framework for correlating isothermal aging to thermal cycling aging. The findings were used to develop the integrated IMC growth model and provide the link between isothermal and thermal cycling aging effects. It is shown that the major contribution of IMC growth during TS and TC aging comes from the high temperature soak or dwell (at 125°C) period. This period can be used to estimate the IMC thickness for typical TS and TC aging profiles used for ATC reliability testing. An acceleration factor, K , is proposed to correlate IMC growth behavior for TC, TS aging to isothermal aging at 125 °C. Failure analysis of lead-free solder joints for PBGA assemblies subjected to thermal cycling aging shows that the growth of IMC thickness and interfacial cracks are dependant on solder joint location in the PBGA assemblies.
2. The elastic modulus and hardness properties of the IMC layer subject to thermal

aging was characterized by a planar IMC surface nano-indentation test method. It was found that the composition change with thermal aging time and causes the elastic modulus and hardness to change as well. Indentation strain-rate dependant hardness and elastic modulus was measured from strain rates of 0.001 to 10 (1/s) for SAC solder. This provide dynamic strain hardening yield stress properties as a function of strain rate suitable for impact drop test modeling conditions where the solder strain rate can reach as high as 10 (1/s).

3. A novel method was developed to measure EM induced back stress by measuring the movement of nanoindentation marker on cross-sectioned FPBGA specimen. The marker motions driven by a combination of EM and back stress were measured at different locations. The distribution of back stress, stress gradient and effective charge number Z^* were calculated. The stress and stress gradient at neutral plane were measured as 9.0MPa and 97 GPa/m, respectively.
4. The combined sequential loading effects of thermal cycling aging and followed by board level drop test for SAC solder assemblies was investigated and reported for the first time. Significant decrease in drop life was observed for both SAC/ENIG and SAC/Cu-OSP soldered assemblies after thermal cycling aging. Kirkendall voids and IMC growth significantly weakened the solder joint interface during TC aging. Drop impact crack path changes from the IMC layer to the IMC/Cu interface. This work shows the great concern of long-term thermal aging on reduction in drop reliability endurance.

8.2.2 Recommendations

Recommendations for future work to improve the developments of failure assessment for Pb-free soldered assembly are as follows:

1. Mathematical models including the consideration of the strain-rate dependant

effects on yield stress from nano-indentation measurement are needed for dynamic plastic modeling of solder joint subject to impact drop loading. Three-dimensional finite element analysis is needed. With the appropriate assumed elastic-plastic input parameters for the indented materials, the simulated indentation load-displacement curve can be used as a comparison to the experimental behavior. Finite element analysis to simulate the deformation behavior during indentation can be investigated and this helps to quantify the accuracy of the measured and predicted elastic-plastic deformation behavior.

2. Nano-indentation marker motion measurement can be applied to measure EM-induced stress and atom motion combined with thermal gradient induced atom migration.
3. Assessment of long term drop reliability of soldered assemblies is needed. Combined loading on reliability is a concern in future, e.g. board drop impact reliability after electromigration and thermal aging exposure.

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Appendix I Solder Joint Specimens

The details for fabrication of solder joint specimen are described in this appendix.

I.1 FABRICATION OF SOLDER JOINT SPECIMENS

For specific test purpose, solder droplet specimen, single BGA SAC solder joint specimen and cross-sectioned BGA specimen from industry were used. Two types of surface finish, Cu-OSP and ENIG with 95.5Sn-3.8Ag-0.7Cu solder were investigated.

I.1.1 Solder droplet specimen

Lead-free solder paste 95.5Sn-3.8Ag-0.7Cu was placed on the FR4 substrate materials covered by a 30 micrometer copper layer with a diameter of 5 mm, as shown in Figure I-1. The ENIG surface finish was plated on copper pad with a nickel (Ni) layer thickness of 5 microns and a gold (Au) flash thickness of 0.3 micron. The FR4 substrate specimen pieces have dimensions of 50mm x 10mm x 2mm. Then the specimens with/without Ni/Au surface finish were reflowed with a well developed temperature profile designed for SAC solder. The peak temperature is 250 °C; reflow time above 217 °C is 120 seconds when the belt speed is 50 cm/min. Different belt speeds 10, 30, 50, 70, 90, 110 cm/min were used for comparison, the reflow times were 600, 200, 120, 86, 67 and 54 seconds, respectively. At each belt speed, 20 specimens were prepared for tests and solid-state aging.

Solder droplet specimens were mainly used to study the solder-Ni(Au)-copper interfacial microstructures, especially the formation of IMC after reflow and thermal aging. Since some tests such as X-ray diffraction need a minimal specimen size, the single BGA specimen cannot be used for XRD measurement.

Figure I-1 Dimension and structure of the solder droplet specimen

I.1.2 Single BGA SAC Soldered Specimen

Compared to solder droplet specimen, the single BGA specimen is more difficult to fabricate. It is used to test IMC growth behavior and the shear and nanoindentation properties. The dimension and structure of the specimen is shown in Figure I-2. It consists of a single BGA 95.5Sn-3.8Ag-0.7Cu solder ball, soldered between two FR4 substrate materials as shown in Figure I-2. The same temperature reflow profile was used to fabricate the specimen, in which only the belt speed of 50 cm/min were used, that is, the reflow time above the melting point 217 °C was 120 seconds. The Ni/Au surface finish on copper pad has a nickel (Ni) layer thickness of 5 microns and a gold (Au) flash thickness of 0.3 micron. The copper pad thickness is 30 microns. The FR4 substrate specimen pieces have dimensions of 12mm x 3mm x 0.5mm.

The single BGA SAC solder joint specimen pieces were placed on a template for soldering. No-clean flux was applied onto the copper pad and a solder sphere is placed on top of the flux and re-flowed on one side as shown in Figure I-3. After the first reflow, another fluxed FR-4 piece is placed onto the template and the re-flowed piece is flipped over a second FR-4 piece and re-flowed for a second time to form a lap shear

specimen. The solder reflow profile with a peak temperature of 250°C was used in the fabrication.

Figure I-2 Dimension and structure of single BGA specimen

Figure I-3 Fabrication Process for Solder Joint Specimen

I.1.3 Solder reflow

The purpose of soldering is to get an electrical, mechanical and thermal connection between the components and the board. The reflow process is achieved using the 8-zone reflow oven as shown in Figure I-4. The increasing temperature in the oven activates the flux. It must then keep the surfaces deoxidized until the wetting of the solder. The reflow profile used in this study was shown as Figure I-5, the specimen were placed on the rolling belt and experience all the temperature zones. As for this temperature profile, when the belt speed was set as 50 cm/min, the reflow time above the melting point 217 °C was 120 seconds. The reflow peak temperature was 250°C. Different belt speeds 10, 30, 50, 70, 90,110 cm/min were used for comparison, the reflow time above 217 °C were 600, 200 120, 86, 67 and 54 seconds, respectively.

Figure I-4 Reflow Oven with 8 heating zones and two cooling zones

The temperature is measured and recorded by a sensor fixed near the soldered specimen. The temperature profile is then read out to computer, the profile is finally optimized to the required condition by adjusting the heaters.

Figure I-5 Temperature profile subject to time with a belt speed of 50cm/minute

The reflow process can be characterized with four different phases: Preheat, Thermal Soak, Reflow and Cool Down. Metallurgical reaction between solder and substrate surface finish forms layers of intermetallic compound (IMC) at the solder/metallization interface. The thickness of the IMC layer depends on factors like temperature of the molten solder and holding time. A long holding time and a high temperature generate thick IMCs.

I.1.4 Other specimens

A 35x35mm square 316 I/O Plastic Ball Grid Array (PBGA) specimen with SAC 387 lead-free solder joint on ENIG surface finish cross-sectioned specimen were used for IMC studies as shown in Figure I-6. FPBGA assemblies with dimension of 15x15mm and 324 I/Os were soldered on PCB board, and were used for thermal cycling aging and drop impact test(See Figure I-7).

Figure I-6 SAC 316 PBGA component and solder balls for the 316 PBGA component

Figure I-7 FPBGA component and FPBGA on PCB board

I.2 ELECTROLESS NICKEL AND IMMERSION GOLD(ENIG)

Nickel and gold layer were mainly used as barrier and protection layer to avoid excess copper consumption during the soldering process, in which gold worked as oxidation/protection layer to avoid the Nickel oxidation before soldering. Nickel is used as diffusion barrier layer to prevent the direct formation of Cu-Sn IMC.

Electroless nickel (Ni) and immersion gold (ENIG) was used in for the single BGA solder joint specimen. Electroless plating (EPL) is a selective autocatalytic metal deposition process based purely on chemical reaction. It's efficient and simplicity benefits lead to substantial reduction in the overall metallization process. The ENIG plating procedure includes the following several steps: a) after surface polishing, residues and oxide remains on the surface of copper. b) An acid solution removes the residues from the surface. c) Native oxide is etched off with a micro-etchant. d) Deposition of Ru metal behaves as a chemical activation for Ni plating. e) Ni is strongly absorbed on the Ru thin film accompanied by dissolution of Ru by simple immersion. f) Ion exchange between Ni and Au ion in the solution. In the whole process, readily available plating solutions (CHEMCAT) were used. A sequence of electroless chemical treatments that cover the copper substrate had been established. Solder was then deposited/placed on the plated surface to complete the multi-layer metallization process.

I.2.1 Initial treatments

KSN-Z2 Acid Cleaner, an acid cleaning process, is designed to remove dust and organic residues from copper as a first stage surface preparation because adhesion and homogeneity of electroless metal deposits suffer if the surface of the base metal is not sufficiently clean. The next step, namely deoxidizing is crucial, because if the native oxide layer is not removed completely from the copper surface, subsequent deposit

becomes non-uniform. A simple wet chemical etching technique such as KSN-SE Chemical Polish/Microetch fitted easily into the process line. This micro-etchant was aggressive enough to penetrate through the tenacious oxide barrier even at room temperature. It produced a leveled surface of uniform texture providing an ideal surface for further processing. The copper substrates were dipped into both KSN-Z2 and KSN-SE for 90 sec and 30 sec respectively.

The copper substrates were then immersed into Planar Pre-initiator XL (Ni initiator). Planar Pre-initiator XL is a metallic immersion coating that ensures complete coverage of copper areas for processing through the planar electroless nickel. Prior to electroless nickel plating, chemical activation of ruthenium (Ru) is necessary since Cu cannot be catalytic to chemicals. This activation process is a critical step which strongly determines the quality of subsequent nickel and gold plating, in terms of the mechanical and electrical integrity. This step had an important effect on the morphology and uniformity of electroless nickel deposits. During Ni plating, the areas with Ru deposit will be sensitized and nickel can then be deposited. The recommended operating conditions were 80-85 °C and 3 min immersion time. This highly acidic solution has a pH level of 0.8. The substrate was withdrawn from the solution, rinsed and dried before the actual plating process.

I.2.2 Electroless Plating

Electroless nickel deposit not only seals the copper surface as a diffusion barrier layer, it also provides hardness, mechanical strength and solderability to the bonding pad. KSN-780 was selected as the electroless nickel-plating solution. The deposit is Ni/P alloy rather than pure nickel. Essentially, nickel was deposited initially by ion exchange or displacement reaction aided by reducing agent. Once initiated, the process autocatalyzed itself to continue nickel deposition at a rate depending on the temperature

and pH of the solution. The plating rate subject to temperature was shown in Figure I-8. For consistent performance, the temperature was maintained at 91 ± 1 °C and the pH (25 °C) at 4.5 ± 0.1 . The plating speed was about 18 ± 2 $\mu\text{m/hr}$ at 90 °C. The substrates were rinsed and dipped into hot de-ionized water before proceeding with Immersion Au plating process using Super MEX #250 Make Up solution. This process was specifically developed for plating onto electroless nickel. It obtained pure gold deposit by ion exchange between substrate metal and Au ion in the solution. Best results and fast initiation of Au plating were obtained using freshly deposited electroless nickel. The measured pH of the solution was maintained at 7.0. The deposition rate is $0.01 \mu\text{m/min}$ at 76 °C. The deposition rate was closely related to temperature; below 65 °C, deposition will decrease and solution will decompose above 80 °C.

Figure I- 8 Effect of temperature on Ni Plating speed of KSN-780

APPENDIX II SPECIMEN CHARACTERIZATION

Some of the important experimental procedure is already included in the corresponding chapters. This appendix provides additional information about the characterization techniques.

II.1 CROSS SECTIONING AND ETCHING

To investigate the microstructure of Solder/UBM interface and solder matrix, the solder specimens was first cold mounted with slow cure epoxy (2 resin + 1 hardener), then ground and polished. The epoxy was poured into the molding cup and cured for 24 h. The hardened mold was then ground using silicon carbide (SiC) paper of grits 800 to remove additional materials and step to the locations to be investigated. When the specimen was ground close to the Solder joints, SiC of grits 1000 was used to grind the materials until the cross-section of solder ball was visible. Next, the sectioned area was polished with the polishing clothes and diamond suspensions of 3 and 1 micron sequentially until the microstructure of the solder could be seen under the optical microscope.

For scanning electron microscope (SEM) observation, the specimen was then etched by the etchant 5% HNO_3 +95%methanol for 15 seconds to make sure the microstructure can be seen under SEM. The specimen were then coated a thin gold or platinum layers to render the sample conductive.

II.2 MORPHOLOGY CHARACTERIZATIONS

The solder cross-sectional morphologies were investigated by a JOEL JSM-5410LV Scanning Electron Microscopy (SEM) under an accelerated voltage 20kV.

Images with magnification of 2000X were captured for microstructure comparison and measurement of intermetallic. But for some specimen, the optical microscopy was also used to capture pictures. Since for some specimens, the IMC thickness measurement must be performed on the optical images, this will be explained at the results sections.

At the same time, Energy dispersed X-ray (EDX) was used to identify the material elements present in each selected area in the solder joint while capturing the SEM images. The working distance (WD) for EDX analysis is 15mm, the spot size is around 1 micron. EDX can be used to detect every element in a particular small area, but it cannot quantitatively give their exact percentage. And thus the composition or phases cannot be determined by this method. However, by combining the EDX results with X-ray diffraction analysis, and phase diagram available from reference, it is not difficult to determine their compositions.

II.3 MEASUREMENT OF IMC THICKNESS

Digital imaging software named Image-Pro Plus (Ver 3.0) was employed in the measurement of the average IMC growth thickness, the principle was shown in Figure II-1. Two polylines R1, R2 were created manually along the edge of the IMC by using the tracing tool. Then the average distance between the two polylines will be given automatically, which is the result of the area divided by the length of the polylines. The thickness results were defined by spatial calibration. The minimum and maximum distance between the two lines will also be marked in the image.

Figure II- 1 Digital imaging techniques to measure the average IMC thickness

For each specimen, 5 different areas were selected and measured; the thickness of the intermetallic was the average of the 5 results. By using the digital imaging technique, the results obtained were quite reliable.

II.4 XRD ANALYSIS

For X-ray Diffraction (XRD) analysis, the apparatus used in the study required a minimal specimen size of 5mm in diameter. The Solder Droplet Specimen mentioned in Section 4.1 was used for XRD analysis. The solder droplet on copper pad was fully etched away (1 nitric acid +1 acetic acid+4 DI water), ultrasonic machine was used to speed up the etching process. After etching, the interfacial system, the intermetallics formed between copper and solder was left and exposed. The phases on the interface were then identified by the X-Ray Diffraction (XRD) analysis on the plane view. The XRD analysis was conducted on a Philips X-pert Powder Diffractometer employing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, DS=0.25°). The X-ray tube was operated at 40 kV and 40 mA. The X-ray diffractograms were recorded at a step size of 0.02° in the range $10^\circ \leq 2\theta \leq 120^\circ$ with 5 s count accumulation per step.

It should be noted that XRD is technique to identify the phases by measuring a series of the crystal inter-planar distance. This is different with EDX, which is used to identify the existence of the element. But with the combination the two techniques, it will be easy to determine the exact phase for an unknown material.

When X-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e. the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. This will result in diffraction where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures called planes.

Most crystals can have many sets of planes passed through their atoms. Each set of planes has a specific inter-planar distance and will give rise to a characteristic angle of diffracted X-rays. The relationship between wavelength λ , atomic spacing (d) and angle θ , shown as in Figure II-2 was solved as the Bragg Equation (or called Bragg law).

$$n\lambda = 2d \sin \theta \quad (\text{II-1})$$

If the illuminating wavelength is known (depends on the type of X-ray tube used normally, the CuK α is used as the illuminating wave, $\lambda=1.5148$) and the angle θ can be measured with a diffractometer then the inter-planar distance can be calculated from the Bragg equation. A set of 'd-spaces' obtained from a single compound will be represent the set of planes that can be passed through the atoms and can be used for comparison with sets of d-spaces obtained from standard compounds database.

Figure II- 2 Radiation effects on crystal planes.

II.5 DIGITAL IMAGE CORRELATION

The principle of the DISA technique is to compare a pair of digital speckle images of a sample before and after loading and to search for the maximum correlation coefficient C

$$C(u, v) = \frac{\sum_{i=1}^m \sum_{j=1}^n [f(x_i, y_j) \cdot g(x'_i, y'_j)]}{\sqrt{\sum_{i=1}^m \sum_{j=1}^n f^2(x_i, y_j) \cdot \sum_{i=1}^m \sum_{j=1}^n g^2(x'_i, y'_j)}} \quad (\text{II-2})$$

where u and v are the displacement components in x and y directions, respectively; $f(x_i, y_i)$ and $g(x'_i, y'_i)$ are the gray-levels at points (x_i, y_i) and (x'_i, y'_i) on the sub-images ($m \times n$ pixels) before and after loading, respectively. A point pair of maximum C is interpreted as the same point on the sample before and after loading. The deformation components are then determined from the coordinates of points (x_i, y_i) and (x'_i, y'_i) .

To improve the search accuracy, two mean values of gray-levels $\bar{f}$ and $\bar{g}$ at points (x_i, y_j) and (x'_i, y'_j) were introduced into the correlation function. Equation (1) can then be rewritten as

$$C(u, v) = \frac{\sum_{i=1}^m \sum_{j=1}^n [f(x_i, y_j) - \bar{f}] \cdot [g(x'_i, y'_j) - \bar{g}]}{\sqrt{\sum_{i=1}^m \sum_{j=1}^n [f(x_i, y_j) - \bar{f}]^2 \cdot \sum_{i=1}^m \sum_{j=1}^n [g(x'_i, y'_j) - \bar{g}]^2}} \quad (\text{II-2})$$

According to the principles of probability and statistics, if the two random variables $f(x_i, y_j)$ and $g(x'_i, y'_j)$ are related, the correlation coefficient distribution of equation (2) has unimodal character and approximate symmetry. It indicates that the improved function is more accurate to find the maximum coefficient. Therefore, a line search algorithm, *i.e.*, searching along the perpendicular direction followed by the horizontal direction, or vice versa, can be employed to replace the above full-field search algorithm for the determination of the peak point.

The real displacement fields should be continuous changed within the calculated area for real structures. But the recognized results usually show discrete and scattered patterns due to correlation errors. And the strains are the partial derivatives of displacement fields; a small error of displacement will cause large error of strain. Thus, it is required to smooth the recognized displacement fields. In order to describe the displacement field in the recognized substructure, one can build an element over the substructure. The displacement field will depend on the node displacement of the element. Based on the discrete values of displacement, one can calculate the node displacement by means of least square method. The target value of least square method will be the sum of difference square between analytical values by element interpolation and the recognized discrete values.

The in-situ micro-deformation in the PBGA solder joints subject to thermal loading were measure by micro digital image speckle correlation system(Micro-DISC), the system is constructed based on the principle of DISA measurement. The system consists of five main parts: a working table; XYZ motorized translation stages; a laser scanning microscope; a miniature thermal cycling chamber; and a computer. Figure 4 shows the schematic system set up.

Figure II- 3 Schematic diagram of micro-digital image correlation system (upper left corner: real image of the system): 1 -- objective lens; 2 -- focus module; 3 -- TV tube; 4 -- zoom module; 5, 7 -- position sensors; 6, 8 -- stepper motors; 9 -- ring light source; 10 -- inner chamber.

The PBGA assembly was sectioned and polished along the symmetric plane and then was put into the miniature chamber. The solder joints located at highly reliability concerned positions-the outmost ones at the corner of the whole BGA (A1,A20, T1, T20), the outmost one located underneath the corner of the silicon die(I9, I12, L9, L12) and some other solder balls were chosen for analysis. Measurements were taken at room temperature 25°C and elevated temperature of 75°C, 125°C. A pair of digital images acquired from an undeformed at room temperature and deformed solder joint at elevated temperature was correlated using the DISA software. The displacement and strain fields were calculated and visualize as images.

II.6 ELECTRON PROBE MICRO ANALYSIS (EPMA)

The composition of the ternary NiCuSn IMC at SAC387/ENIG interface before and after thermal aging and EM test were quantitatively determined by electron probe micro analysis (EPMA). The electron microprobe is designed specifically for detecting and measuring characteristic X-rays. It uses an electron beam current from 10 to 200 nanoamps, roughly 1000 times greater than that in a scanning-electron microscope

(SEM). These higher beam currents produce more X-rays from the sample and improve both the detection limits and accuracy of the resulting analysis. The resulting data yield *quantitative* percentage and thus the ratio of Ni, Cu and Sn atoms in the ternary IMC.

Solder joints were cross-sectioned for analysis. The representative interface morphology of the IMC and the corresponding concentration curves of Ni, Cu and Sn are given in Figure II-4 and Figure II-5.

Figure II-4 SAC/ENIG single BGA solder joints

Figure II-5 EPMA analysis curves and elements distribution of Ni, Cu and Sn (a) combined curve (b)Sn, (c) Cu, (d) Ni, (e) P, (f)Ni

A typical EPMA result for the mass percentage and atomic ratio is given in Table II-1 for Ni(P) layer and NiCuSn IMC in as-reflowed solder joint. The mass concentration of phosphors in Ni(P) layer is 6.1%. The composition of NiCuSn IMC layer is $(\text{Ni}_{0.28}\text{Cu}_{0.72})_6\text{Sn}_5$ for this test point.

Table II-1 Representative EPMA analysis of SAC387/ENIG solder joint (as-reflowed)

Ni(P)		P	Ni	Total	
		Mass percent	6.132	92.46	98.592
NiCuSn	Atomic Ratio	11.1678	88.8322	100	
		Ni	Cu	Sn	Total
	Mass percent	10.088	28.567	61.916	100.571
	Atomic Ratio	15.0327	39.3277	45.6396	100

APPENDIX III PROPERTIES OF PACKAGING MATERIALS

Some of the important physical, mechanical and electrical properties of most commonly used materials in electronic packaging are summarized in this appendix.

Table III-1 Properties of bulk solder alloy*

Properties	Sn-37Pb	Sn-57Bi	Sn-3.5Ag	Sn-5Sb	Sn-0.7Cu	Sn-9Zn	Sn-3.8Ag-0.7Cu
Melting Temperature(°C)	183	139	221	238	227	199	217
UTS (MPa)	31-46	45-80	55	23-42	31	60-65	50-70
Elongation (%)	35-176	40-200	35	90-350	12	8	50-120
Shear strength(MPa)	28.4	48.3	32.1	31.8	/	/	/
Hardness (HV)	12.9	20	17.9	17.2	14.4	23	/
Elec. Resistivity ($\mu\Omega$ cm)	17.0	30-35	7.7	17.1	10-15	10-15	8-12
Elastic modulus	29	35	37	58	/		50
Fracture Toughness (MPa-m ^{1/2})	8.36	/	4.7-11	6.7-9.6	/	/	/

Sources:

P284, Table 2, 3 of “Handbook of lead-free solder technology of microelectronic assemblies, Sung K. Kang, edited by Karl J. Puttlitz and Kathleen A. Stalter. Marcel Dekker, New York, 2004”

Table III-2 Properties of Sn, Cu, Ni and their Intermetallics

Properties	Cu	Sn	Ni	Cu ₆ Sn ₅	Cu ₃ Sn	Ni ₃ Sn ₄
Fracture toughness (MPa-m ^{1/2}) K _{IC}	30-	4.7-11	80-100	1.4	1.7	1.2
Elastic Modulus (GPa)	117	30-40	213	85.6	108	133
Thermal expansion x 10 ⁻⁶ /°C	17.1	23	12.9	16.3	19.0	13.7
Elec. Resistivity (μΩ cm)	1.7	11.5	7.8	17.5	8.93	28.5
Density gm/cc	8.9	7.3	8.9	8.28	8.9	8.65
Thermal conductivity watt/cm-deg	3.98	0.67	0.905	0.341	0.704	0.196

Sources:

1. Page 60-61 in “The mechanics of solder alloy interconnects, Darrel Frear (edit), Chapman & Hall, New York, 1994”
2. Page 59 in “Materials Selection in Mechanical Design, Third Edition, Michael F. Ashby, London 2005”
3. Page 123-125 in “Solder Joint Reliability of BGA, CSP, Flip Chip and Fine Pitch SMT Assemblies, John H. Lau and Yi-Hsin Pao, McGraw-Hill, 1997”

APPENDIX IV PUBLICATIONS

The following journal papers are related to the present research:

- [1] **Luhua Xu**, John H.L. Pang and K.N. Tu, Effect of electromigration-induced back stress gradient on nano-indentation marker movement in SnAgCu solder joints, *Applied Physics Letters*, 89, 221909, 2006
- [2] **Luhua Xu** and John H.L. Pang, In-Situ Electromigration Studies on SnAgCu Solder Joint by Digital Image Speckle Analysis, *J. Electronic Materials*, 2006 (35-11): 1993
- [3] **Luhua Xu**, John H. L. Pang, Fei Ren, K. N. Tu. “Electromigration Effect on Intermetallic Growth and Young's Modulus in SAC/ENIG Solder Joint” *Journal of Electronic Materials*, 2006 (35-12):2116
- [4] **Luhua Xu**, John H. L. Pang, “Nanoindentation on SnAgCu and SnCu Lead-Free Solder and Analysis” *Journal of Electronic Materials*, 2006 (35-12): 2017
- [5] **Luhua Xu** and John H.L. Pang. “Nano-Indentation Characterization of Lead-Free Solder and IMC layer Properties”. *Thin Solid Films*. 2006 (504):362.
- [6] **Luhua Xu**, John H. L. Pang, Kithva H. Prakash. “Isothermal and Thermal Cycling Aging on IMC Growth Rate in Lead-Free and Lead-Based Solder Interface”. *IEEE Transactions, Components and Packaging Technologies* 2005(28):408
- [7] John.H.L Pang and **Luhua Xu**. “Intermetallic Growth Studies on Sn-Ag-Cu Lead-Free Solder Joints”. *Journal of Electronic Materials*, 2004 (33-10): 1219
- [8] Fei Ren, Jae-Woong Nah, K. N. Tu Bingshou Xiong, **Luhua Xu**, and John H. L. Pang Electromigration induced ductile-to-brittle transition in lead-free solder joints *Applied Physics Letters* 89, 141914 ,2006