A STUDY ON MECHANICAL BEHAVIOUR OF LEAD-FREE SOLDER USING NANOINDENTATION TEST

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Abbreviations

305 SAC	Sn-3.0Ag-0.5Cu
IMC	Intermetallic Compound
IML	Intermetallic Layer
EU	Europe Union
PCB	Printed Circuit Board
RoHS	Restriction of Hazardous Substance
NEMI	National Electronic Manufacturing Initiative
SMT	Surface Mounting Technology
SEM	Scanning Electron Microscope
EDX	Electron Dispersive X-ray

Abstrak

Oleh sebab penggunaan komponen plumbum telah dihadkan oleh Eropean Union, penggantian Sn-Ag-Cu diselidiki dan diamalkan dalam bidang pembuatan elektronik. Dengan dorongan berterusan untuk pengecilan size dalam pakej elektronik, kekuatan pateri bersama komponen elektronik di papan litar dikurangkan disebabkan oleh penurunan kawasan hubungan. Oleh itu, sifat mekanikal yang dipertingkatkan bersama sendi pateri oleh nanopartikel diperkenalkan untuk menyokong perubahan teknologi. Tujuan kajian ini adalah untuk mengkaji kesan tetulang nanopartikel ke dalam pateri nanokomposit pada a) struktur mikro dan ketebalan lapisan gabungan intermetallik b) modulus kekerasan dan anjal lapisan sebatian intermetallik dan pateri nanokomposit. Dalam kajian ini, 0.05wt% TiO_2, Fe_2O_3 dan NiO nanopartikel bercampur dengan pes pateri. Dengan menggunakan teknologi pemasangan permukaan, kapasitor diletakkan pada pes pateri bercetak pada papan litar bercetak sebelum pematerian. Kemudian, sampel disediakan dalam papan litar bercetak yang dipotong dengan resin keras. Ciri mekanikal diukur dengan menggunakan eksperimen nanoindentation dan pemerhatian pada permukaan sampel dicatatkan. Penguatkan nanopartikel telah menyebabkan perubahan morfologi lapisan intermetallik dan 23% - 28% pengurangan ketebalan lapisan intermetallik. Modulus kekerasan dan elastik pateri nanokomposit meningkat sebanyak 1% - 11% dan 8% - 31% masing-masing. Pada kesimpulannya, pengukuhan nanopartikel ke dalam pateri komposit telah meningkatkan ciri mekanikal nanokomposit pateri dan dengan itu menguatkan sendi pateri.

Abstract

As the usage of lead components has been limited by Europe Union, replacement Sn-Ag-Cu is investigated and practiced in the electronic manufacturing field. Due to constant push for miniaturization in the electronic package, the strength of solder joint of the electronic component on circuit board is reduced due to the decrease in the contact area. Therefore, enhanced mechanical properties of solder joint by embedding nanoparticles are introduced to support changes in technology. The aim of the study is to investigate the effect of nanoparticles reinforcement into nanocomposite solder on a) microstructure and thickness of intermetallic compound layer b) hardness and elastic modulus of the intermetallic compound layer and nanocomposite solder. In this study, 0.05wt% of TiO_2, Fe_2O_3 and NiO nanoparticle is mixed in solder paste respectively. By using surface mounting technology, miniaturized capacitors are placed on printed solder paste on printed circuit board before reflow soldering. Then, samples are prepared in cold mounted sectioned printed circuit board. The mechanical characteristic is measured by using nanoindentation experiment and observation on the sample surface is recorded. The reinforcement of nanoparticles has caused the changes of morphology of IMC layer and 23% - 28% of thickness reduction of the IMC layer. The hardness and elastic modulus of nanocomposite solder are increased by 1 % - 11% and 8% - 31% respectively. In the conclusion, reinforcement of nanoparticles into composite solder has improved the mechanical characteristic of nanocomposite solder and thus strengthen the solder joint.

Chapter 1 Introduction

1.1 Research Background

For decades, lead-tin solder has been used in microelectronic industry to attach the microelectronic components on Printed Circuit Board (PCB). Lead-tin solder (63% tin to 37% lead) is an ideal composition to use due to its melting point at 183oC which is suitable for electronic components to prevent high strain due to high heating temperature during the assembly process.[1] However, in Restriction of Hazardous Substance (RoHS) 1st July 2006, European Union has restricted the maximum levels for lead (Pb) to lower than 1000ppm due to the human health and environment issue.[1] Thus, termination of usage of lead in electronic industry is compulsory and investigation on propose of potential material to replace lead in solder paste is beginning.

By referring to a set of criteria in replacing Sn-Pb alloy, National Electronic Manufacturing Initiative (NEMI) has chosen Sn-Ag-Cu system and specifically to Sn-3.9 Ag-0.6Cu (±0.2%) in the Sn-Ag-Cu (SAC) family of alloys as the most promising surface mount alloy solution.[2] Changes in the physical and chemical properties of the new combination alloy have been emphasized on the temperature required to form a proper intermetallic bond. The melting point for most widely used leaded alloys such as Sn-60 Pb-40 is 183oC while for common used lead-free alloy, Sn-95 Ag-3.0 Cu-0.5 (SAC 305) has the melting point of 217oC to 220 oC. [3] The transition of the melting point is a crucial point for intermetallic bond formation in the reflow process.

Reinforcement of lead-free solder with nanoparticles

The idea of reinforcement of nanoparticle in lead-free solder is introduced to enhance mechanical properties of SAC that found not ideally in some aspect that would reduce the strength of solder joint. By the addition of nanocomposite material, some mechanical performance of lead-free solder is modified into a new structure of the compound and give impact in the electronic packaging industry. The nanoparticles that have been studied include Ag, ZrO2, Co, Al2O3 and TiO2 and the changes on the mechanical characteristic of reinforced solder such as melting temperature, wettability, hardness and tensile strength is commonly investigated. [4]

Surface Mounting Technology

The electronic components surface mounting technology (SMT) is the electronics assembly process where electrical component is joined to PCB via individual pad connections located on the board surface [5]. The most important steps of SMT in the quality decision of component mounting is solder reflow. In the process, electronic components attach with solder paste to PCB by applying a certain range of temperature and time. There have few phases in solder reflow process which are pre-heat, soak, reflow and cooling phases. The temperature in reflow process has to be controlled properly which is not suggested to over the certain range of material melting point to prevent failure or defects caused such as harden, burn of solder, damage of electronic components. Besides that, time of reflow process is significant for the intermetallic layer between solder paste an individual pad. Excessive soldering temperature and time speeds the interfacial reaction and makes IMC grow more severe which result in decreased strength of solder joint.

Miniaturization of Electronic Packages

The demands on the smaller size and lighter-weight especially electronic products drive towards miniaturization in next-generation electronic components and systems. The demands for smaller parts is coming from both the need for smaller assemblies in specific applications and the need to reduce material costs. The smaller size of electronic products has led to the miniaturization of electronic components such as a capacitor. Over years of development in nanotechnology, size of capacitors is getting smaller which changing from 2512 to 01005. However, there is a lot of technology has to be invented to support down-size effect to ensure there is further development in miniaturization of electronic packages.

Mechanical Properties of Intermetallic Compound Layer of SAC

Solder joint between electronic components and individual copper pad on printed circuit board (PCB) composed of 3 parts, i) intermetallic compound layer between the solder and copper pad ii) intermetallic compound distribute in solder and iii) bulk solder. During the solder reflow process, the metallurgical reaction between solder and copper pad forms a layer of the intermetallic CuxSny compound between copper pad and solder. Mechanical properties of joint strongly depend on the characteristics of intermetallic layer and solder. IMC layer formation is beneficial for joint bonding between solder and substrate, however, due to general mechanical properties of brittle IMC, it might lead to joint fracture. Thus, the thickness of IMC layer is a decisive parameter that might lead to degradation of joint strength due to low fracture toughness and brittle in nature. [6] Recently, there has researches study on the effect of the reinforcement of nanoparticles into SAC on the mechanical properties of the IMC layer which generally concern on the hardness, modulus, and suppression on the growth of IMC layer. Researchers are still continuing to find out the optimized solution for the solder joint.1.2

1.1 Problem Statement

As the restriction on usage of lead components has been announced, the transition from leaded solder to lead-free solder is forced to execute and here SAC is introduced. However, cases of failure of solder joint which due to the brittle natural behavior of intermetallic compound layer formed have greatly reduced product reliability. There are few researchers proposed that thick intermetallic layer between the interface of bulk solder and individual pad reduced the tensile strength and shear strength of the solder joint.[7] Besides that, microvoids in IMC layer has acted as crack initiator and propagates randomly in the brittle layer and thus cause fracture and failure of the solder joint. Furthermore, due to the constant push of miniaturization in electronic packages, it rises an issue of reduction of size solder joint formed between miniaturized electronic component and circuit have leads to decrease in strength of solder joint. Therefore, the mechanical properties of solder have to be improved to increase the reliability of solder joint and thus the idea of reinforcement of nanoparticle in nanocomposite solder is used.

1.3 Research Objective

1. To study the effect of reinforcement of nanoparticles in solder paste on microstructure and thickness of IMC layer in solder joint.
2. To investigate the effect of reinforcement of nanoparticles in solder paste on hardness and elastic modulus of IMC layer and bulk solder.

1.4 Scope of Work

The scope of this project will be divided into 2 sections which are experiment and analysis. From the previous study, the strength of solder joint is highly correlated to mechanical properties of IMC layer and nanocomposite solder. Therefore, investigation of hardness, elastic modulus, microstructure morphology and thickness of IMC layer is done on pure 305 SAC. However, due to the idea of nanoparticle-reinforced solder is proposed, the effect of reinforcement studies. Thus, the same experiment is done on another 3 nanoparticle reinforced solder to compare the changes in this aspect due to different material nanoparticle reinforced.

In this study, 4 samples which are 305 SAC (SnAgCu), 305SAC- TiO2, 305 SAC- Fe2O3 and 305 SAC- NiO specimens are undergoing the nanoindentation test in the laboratory. From result proposed from a previous study [8], the lowest thickness of IMC layer in SAC-TiO2 is achieved at 0.05wt% of TiO2. Therefore, 0.05wt% is chosen to be a standard concentration of nanoparticles reinforced in this study and comparison is done to investigate the mechanical behaviors of different materials at this concentration.

The inspection of hardness and elastic modulus of micron-size IMC and solder bulk solder are conducted using nanoindentation technique. The solder joint inspection of electronic components is commonly done by using nano-scale indentation with Berkovich indenter. Berkovich indenter is a three-sided pyramid which different angle of the side of the pyramid which is 76.9o and 65.3o as shown in Fig.1.1. The popularity of the Berkovich indenter is due to its feature as i) it has a constant area-to-depth ratio that yields a hardness value that is independent of the load applied. ii) it is sharper than others indenter and the sharpness enables measurement of the smaller possible testing volume which is suitable for nanoindentation. The structure of bulk solder and indentation mark will be observed by using Scanning Electronic Microscope (SEM) for data analysis and Energy Dispersion X-ray spectrum (EDX) to observe the distribution of compound in the solder joint.

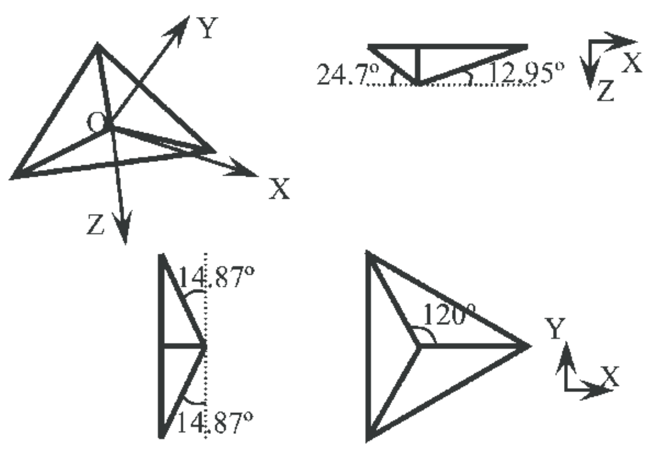


Figure 1.1Dimensions of Berkovich Indenter [9]

Chapter 2 Literature Review

2.0 Overview

Due to the formation of the brittle behavior of intermetallic compound layer and bulk solder phase in the solder joint, fracture or failure of the solder joint is a concern of research. Therefore, there are varies experiments and testing done on mechanical properties such as hardness, elastic modulus, tensile strength and shear strength of nanocomposite solder and IMC layer to determine the reliability of the solder joint. However, the researchers on improvement on stable and strong solder joint are switch to the reinforcement of nanoparticles in solder. Addition of stable, non-reactive oxides is preferred to investigating the effects of nanoparticles on solder joint strength. In this chapter, several works of literature on mechanical properties of SAC solder paste and reinforced nanocomposite solder are reviewed.

2.1 Formation of intermetallic compound layer (IMC)

Surface mounting technology is used in the electronic assembly process. The solder paste is print on printed circuit board, electronic components put on the position then thermal reflow is done. During the wetting process, thermal energy is applied and copper dissolute from the copper substrate is diffuse into tin Sn-rich phase to form initial IMC layer of Cu6Sn5 at the interface of the copper substrate and liquid solder matrix. The intermetallic compound in solder matrix and at the interface of solder paste/Cu nucleate continuously during cooling and did not only occur in the first stages of cooling as commonly occurs in the solidification of alloys. [10] The thickness of IMC layer formed depends on the concentration and distance Cu atoms traveled into solder matrix. The formation of IMC layer is observed by in-situ real-time imaging under high magnificent.[11] From the research done by M.A.A.Salleh and et al, the Sn-0.7wt% Cu solder matrix is reflow and real-time imaging on IMC and solder void formation at the interface is recorded as shown in Fig.2.1. From Fig.2.1 shown, the thickness of IMC layer has a positive correlation with aging time. Due to a higher driving force for precipitation at the metastable solder/substrate interface, this planar g-Cu6Sn5 layer tends to form during the early stages of soldering compared to the ε-Cu3Sn formation, which forms at a later stage in a subsequent reaction.

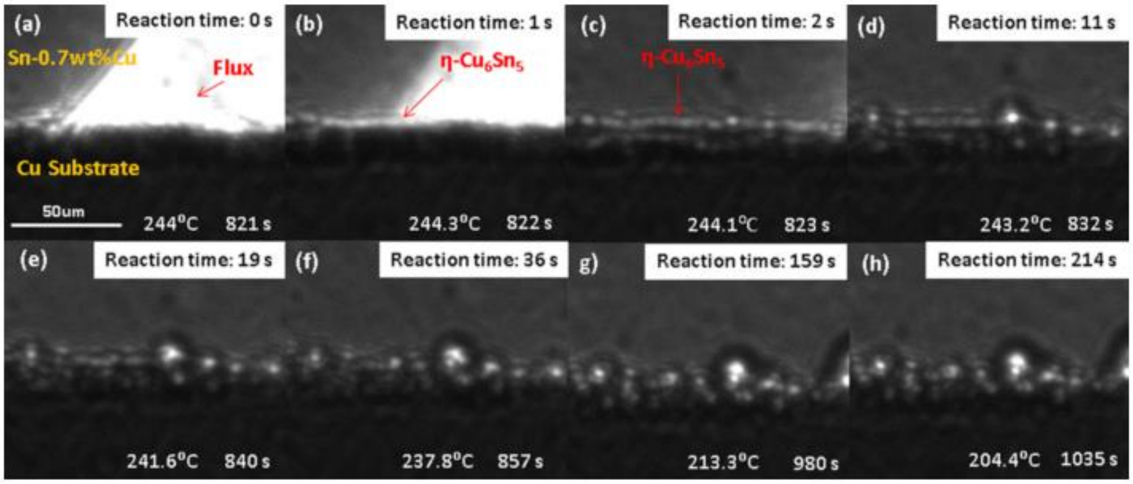


Figure 2.1 High magnification in situ real-time imaging observations of solder voids and IMC formation between Sn–0.7 wt.% Cu and Cu substrate interface at (a) 821 s, (b) 822 s, (c) 823 s, (d) 832 s, (e) 840 s, (f) 857 s, (g) 980 s and (h) 1035 s of experiment time [10]

As shown in Fig.2.2, three different growth mechanisms have occurred, with n = 0.07 at 1–10 s of reaction time, n = 0.31 at 10–50 s of reaction time and n = 0.03 at 50–270 s of reaction time indicate that the IMC layer growth rate different at different reaction time.

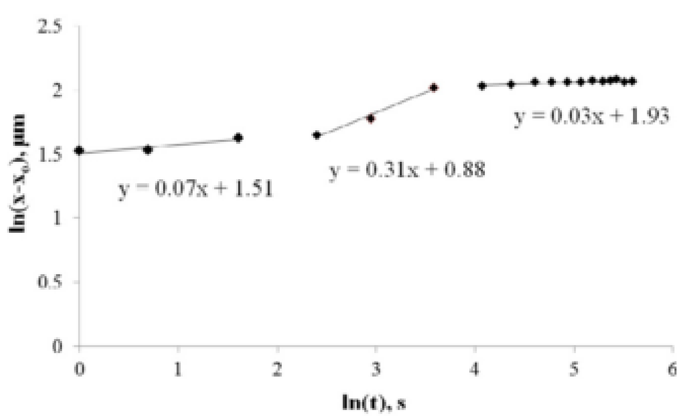


Figure 2.2 Log plots of IMC growth taken subsequent to the synchrotron experiments. [11]

Void and bubbles formed by flux outgassing exist at melting process. Void have an irregular shape and develop into spherical shape to minimize the interfacial area between solder/Cu. [10]

2.2 Mechanical characteristic of lead-free solder joint

In order to investigate the reliability of solder joint, the researcher has done experiments on solder joint to determine its mechanical characteristic which the common properties are microstructure, hardness and elastic modulus of solder and IMC layer. For lead-free solder paste of SAC, the solder joint might composed of solder, Cu_6Sn_5, Cu_3Sn, and Ag_3Sn. The advanced development of electronic manufacturing industries has created the even smaller size of electronic components which in nano-scale. Therefore, elastic modulus and hardness of lead-free solder joint are inspected using nanoindentation technology. R.R.Chromik and et al, have done nanoindentation on solder joint SAC 305 with a maximum load of 2mN on solder, Cu_6Sn_5, Cu_3Sn, and Ag_3Sn. The result from the research is listed in Table 2.1. This research proposed that Cu6Sn5 has the highest hardness among 4 alloys and conclude that Cu-Sn has brittle behavior while Ag_3Sn has ductile behavior. [12]

Table 2.1Measurement of the Indentation Modulus and Hardness for the Four Alloys Studied [12]

Material	Indentation Modulus (GPa)	Hardness (GPa)
Cu_6Sn_5	134 ± 7	6.5 ± 0.3
Cu_3Sn	160 ± 8	6.2 ± 0.4
Ag_3Sn	99 ± 5	2.9 ± 0.2
SAC solder	51 ± 8	0.16 ± 0.06

Meanwhile, continuous stiffness measurement (CSM) nanoindentation technology has also used to measure hardness and elastic modulus of the solder joint. The hardness and elastic modulus are updated continuously from the first moment until the end of indentation. [13] However, the hardness and elastic modulus of IMC layer of 305 SAC in research of Yuan and et al are greatly different from the previous experiment. The hardness and elastic modulus of IMC layer are 1.16GPa and 90GPa while for solder are 0.78 GPa and 57.8 GPa. This would be due to the external factor that contributes to a different result obtained. The statement is validated with research of S.Lotfian and et al, which hardness and elastic modulus of IMC layer is 6.7 ± 0.4 GPa and 117 ± 5 GPa while for solder are 0.31 ± 0.01 GPa and 52 ± 6 GPa.[14]

In SMT technology, a reflow process is important information of IMC layer and structure of solder matrix. Creep in materials is one of the thermal-dependent mechanical properties that would affect the fracture of solder bonding. Therefore, aging period and temperature become important parameters in optimization research. The thermal energy given to solder joint is responsible for dissolution and diffusion of Cu atom with Sn-atom to form Cu-Sn IMC layer only. Therefore, with constant reflow temperature, same IMC compound is formed in solder joint and thus aging periods has no effect on the hardness of the IMC layer. [15] However, creep behavior of material affect other experimental parameters such as loading rates, maximum load applied and dwell time. By decrease loading rate on nanoindentation, there has enough time for dislocation of grain boundary occurs which well-known as creep effect. As the same time, due to dislocation and sliding of the grain boundary with time, strain-rate hardening effect results in a different hardness of the material. This explanation is also applicable to the aspect of a maximum load applied and dwell time. Both have a positive correlation with creep effect on the material. It can be observed by using CSM indentation technology that decreases the hardness of the material as dwell time increased with creep loading as shown in Fig.2.3. [16]

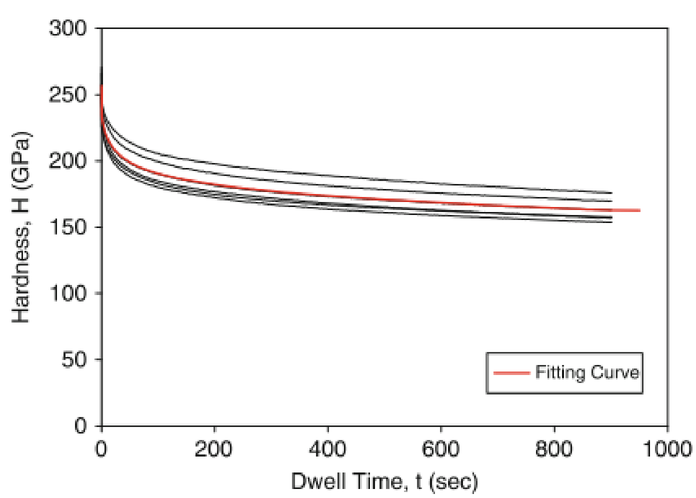


Figure 2.3 Hardness versus dwell time for SAC305 solder during nanoindentation creep loading. [17]

Besides testing on hardness and elastic modulus, fracture research continues on microstructure and thickness of IMC layer and solder phase. Microstructure and thickness of IMC layer result significant effect on tensile strength of solder bond and thus affect the fracture of joint. [7] Tong and et al done tensile strength test on solder joint by solder 2 copper plate together as shown in Fig.2.4.

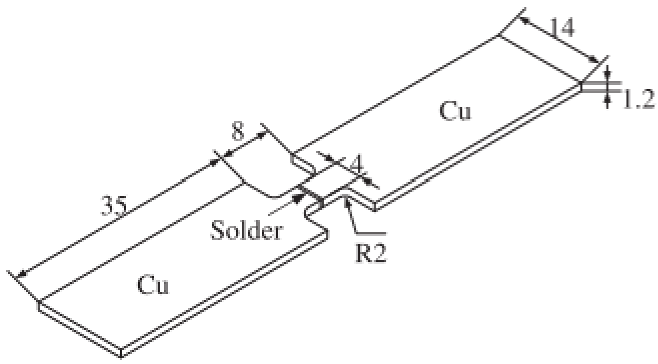


Figure 2.4 Geometry of the tensile test sample of the solder joint (unit: mm)[7]

The sample is aging in isothermal at 150 oC for 0, 72, 288 and 500 h. The shape of Cu6Sn5 from changes elongated scallop-shape at 0s to planer-layer shape at 500h. During aging period, more Cu atom is diffuse with Sn matrix at a deep channel of elongated-scallop of IMC layer, thus filled the deep channel of IMC layer and form more uniform and thicker planer layer. Due to the formation of void and bubbles at the interface of IMC layer, it becomes the crack initiator and micro-cracks formed in IMC layer. At longer aging time, the micro-cracks in IMC layer is increase and elongated scallop shaped of IMC which act as crack propagator is reduced.

By taking consider of strain rate effect in fracture testing, it is observed that fracture modes have been transit from ductile to brittle behavior. This is because dimples in ductile solder need longer time to form compared to micro-crack in IMC layer. The fracture mode in solder joint is changed from ductile to brittle behavior as aging temperature and strain rate increase as shown in Fig. 2.5 and Fig.2.6 [7] The dimples portion is getting lesser and area of broken Cu6Sn5 is increased. This indicates that fracture mode of the solder joint is affected by an aging effect.

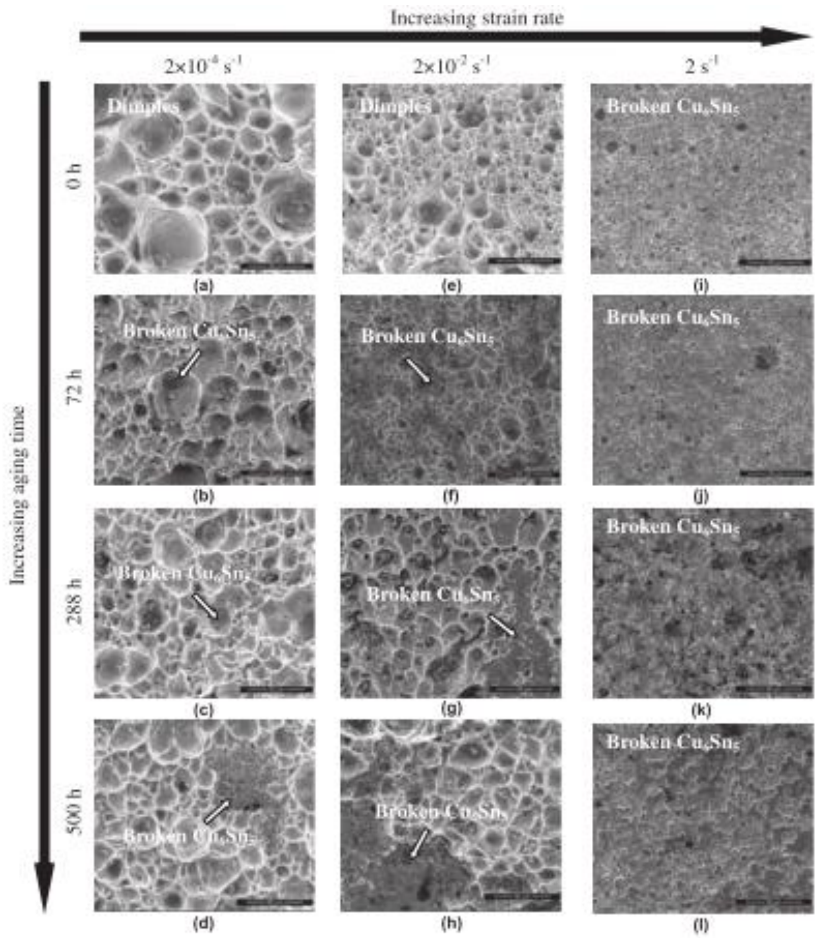


Figure 2.5 SEM images of the fractured surfaces of the solder joints aged for different time and tested at different strain rates [7]

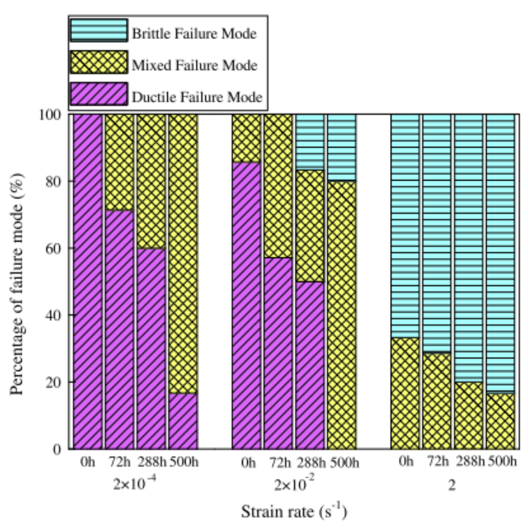


Figure 2.6 Distribution of the three failure modes occurred in the solder joints aged for different time and tested at different strain rates. [7]

In investigate the mechanical properties of material, it couldn't omit the effect of grains orientation of material. It is believes that solder joint has anisotropic characteristic which is orientation dependent. [18] The joint orientation is understand vigorously by using, Electron Backscatter Diffraction (EBSD). The results show there has 2 different hardness and elastic modulus value for 2 different solder joint orientation. Same theory is validated result of research done by V.M.F. Marques and et al, who investigation on effect of orientation on mechanical properties of solder joint. [17] Therefore, nanoindentation done on solder joint should consistently in single directions to avoid error in result comparison.

2.3 Reinforcement of nanoparticles in solder

After investigation on several factors that effect on strength of solder joint, researchers look for new solution to optimize the solder matrix and strengthen the bonding of electronic components on PCB. Varies of nanoparticles such as Ni, Zn, Al and Ag are added in solder to study the changes on microstructure, mechanical properties and fracture strength of solder joint. Recently, the trend of nanoparticles reinforce of research has changes to non-reaction oxide compound. In this research, effect of reinforcement of nanoparticles of TiO_2, Fe_2O_3 and NiO in solder on hardness and elastic modulus of nanocomposite solder and IMC layer is studied.

2.4 Reliability of solder joint with TiO_2 nanoparticle reinforcement

The nanoparticle of titanium dioxide, TiO_2 is mix in solder evenly and print on board. When heat applied, the reaction or changes on composite solder and IMC is studied. From several researchers states that nanoparticles of TiO_2 inhibit the growth rate of the Cu_6Sn_5 layer and refine the IMC Ag_3Sn in composite solder. [19]–[22] Microstructure of IMC layer and composite solder is changes by addition of the different percentage of TiO_2. In research of Tang et al, the microstructure of IMC layer changes from elongated scallop shape at 0 wt% TiO_2 to round continuous scallop at 0.5 wt% and lastly to wicked shape Cu_6Sn_5. [19] The wicked shape of IMC layer into composite solder has high-stress concentration focus and act as a crack initiator that lead to failure of the solder joint. The reaction with nanoparticle TiO_2 will form a stable compound which has lower surface energy than entangled with each other. Therefore, Ag_3Sn in solder reacts with TiO_2 and size and spacing of compound is refined as shown in Fig.2.4. The refined Ag_3Sn compound and TiO_2 is precipitated on the grains boundary of IMC Cu-Sn layer, act as a diffusion barrier to reduce the diffusion of Cu atom into the Sn-rich solder, thus the thickness and growth rate of IMC layer is reduced as the percentage of TiO_2 increased. However, the thickness of IMC layer will increase when the percentage of nanoparticles over the critical amount.

The thickness of IMC layer increased at 0.6 wt% in Tang et al's research [19] and 0.15wt% in Yahaya et al's research.[22] This is due to saturated Ag_3Sn at the interface of IMC/composite solder has coarsened the Ag_3Sn precipitated on IMC layer. The theory is verified by Yahaya et al who state claimed that the TiO_2 nanoparticles is agglomeration and segregated, entangled with each other by van der Waals forces. The entangled TiO_2 deposited on larger grains Cu_6Sn_5 IMC in solder matrix due to Gibbs-Thomson effect. Therefore, the suppression on the growth of IMC layer is reduced and thickness of IMC layer is increased. [8]

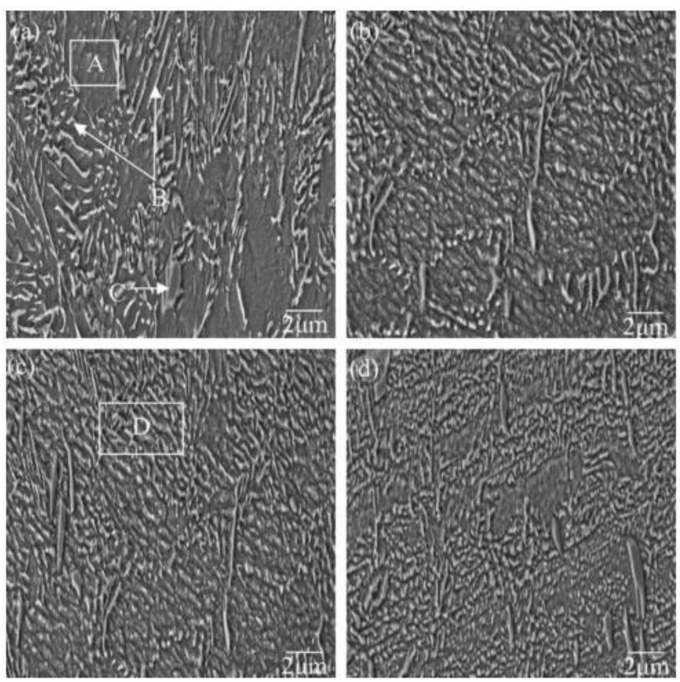


Figure 2.7 SEM micrographs of microstructure in Sn–3.0Ag–0.5Cu–xTiO2 composite solders reflowed for 60s: (a) x = 0 wt.%; (b) x = 0.05 wt.%; (c) x = 0.1 wt.%; (d) x = 0.6 wt.%. [22]

Besides that, the refinement of Ag_3Sn has enhance the shear strength of solder joint. The pinning mechanism of Ag_3Sn and nanoparticle on grain boundary of IMC layer has impede to dislocation and sliding of grains, increase the shear force act on it. Shear strength of solder joint is increase with addition of nanoparticle TiO_2. However, the excessive addition of TiO_2 will reduced the mean shear strength due to coarsen of Ag_3Sn.Thickness of IMC layer and shear strength has negative correlation as shown in Fig.2.8 due to pining mechanism and refinement of Ag_3Sn compound.

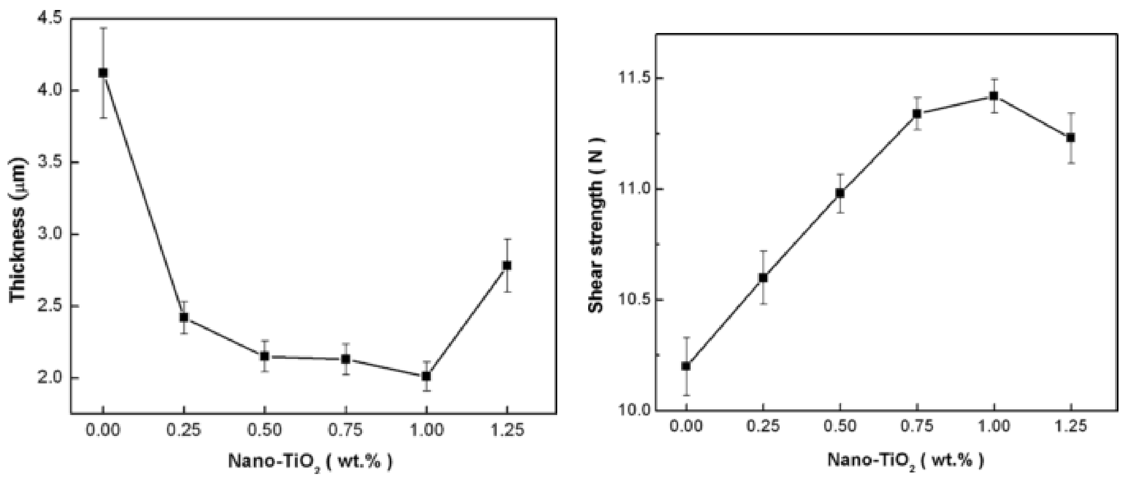


Figure 2.8 a) The thicknesses of Cu6Sn5 IMC layers at the solder/pad interfaces of the Sn3.5Ag0.5Cu composite solder packages versus added wt% of nano-TiO2 b) Ball Shear strength of Sn3.5Ag0.5Cu composite solder joints [23]

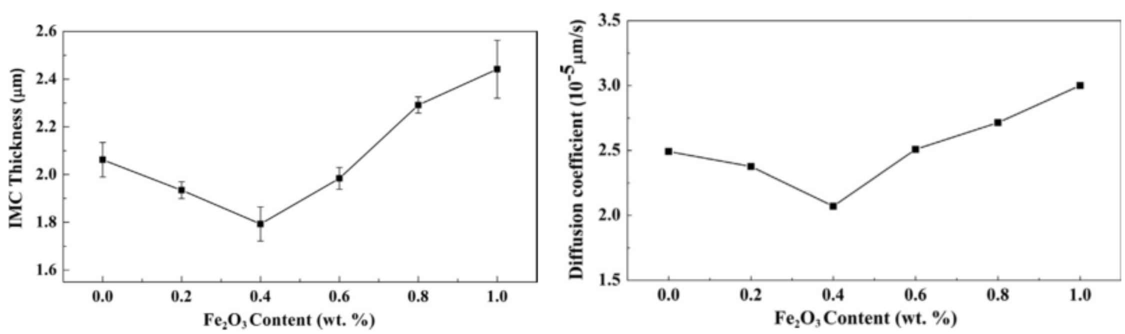
Besides that, addition of nanoparticle also increase the hardness of composite solder. Distribution of TiO_2 in composite solder is act as nucleation side and precipitated on grain boundary and pining mechanism of refined Ag_3Sn impeding slide and increase the dislocation density and obstacles to motion of grain. Thus, higher load is applied and hardness of composite solder is increase with addition of nanoparticle. Chemical reaction in composite solder has increase the formation of micro-void, which leads to decrease of ductility of composite solder. [21]

2.5 Mechanical properties of solder joint with Fe_2O_3 nanoparticle reinforcement

There are few researches that focus in study of changes and strength of solder joint. The Cu atoms from the copper pad dissolution will react with the Sn atoms in the lead-free SAC305-x Fe_2O_3 nano- reinforced lead-free solder paste to form an intermetallic phase called Cu6Sn5 which is a metallurgical bond occurring in the boundary between the solder and the copper pad on the OSP substrate during the reflow soldering process. Similar to

TiO_2, the addition of nano Fe_2O_3 particles in solder enables the retaining of growth of IMC layer. [24]–[27] Yue et al have done experiment with addition of 0, 0.2, 0.4, 0.6, 0.8, 1 wt% Fe_2O_3 in solder matrix. As shown in Fig.2.9, the IMC thickness is decreased until minimum at 0.4 wt% of Fe_2O_3 then increase beyond it. The diffusion coefficient of IMC layer has similar trend of graph with thickness. [24]

To the nanoparticles in the molten nanocomposite solder, they either adsorb on solid surface or agglomerate to transform into large size particles in order to minimize their surface energy. When slight amount of Fe_2O_3 nanoparticles were added into the SAC107 solder, the nanoparticles trended to adsorb to the surface of interfacial IMCs or Cu substrates in order to minimize the surface energy. Nanoparticles adsorbed on the surface of the Cu substrate act as diffusion barrier and impede the reaction and the inter-diffusion of Sn and Cu atoms, which decrease the interfacial IMC thickness and slow down the IMC growth during isothermal aging as shown in Fig.2.7. The small size of nanoparticle adsorb on the IMC layer which is low surface energy has better suppression effect on interfacial IMC formation. Larger size particle difficult to adsorb on surface due to their lower surface energy and larger size particles will increase the crystal lattice defects of interfacial IMC layer and accelerate the diffusion between Sn and Cu.[25] However, with excessive addition of Fe_2O_3 nanoparticle, the nanoparticles agglomerate and transform into large particles and thus decrease the retaining on growth rate of IMC layer.



a b

Figure 2.9 a) Average thicknesses of interfacial IMC layer versus nano-Fe_2O_3 content after reflow b) Growth rates of interfacial IMC layer versus nano-Fe_2O_3 content during isothermal aging. [24]

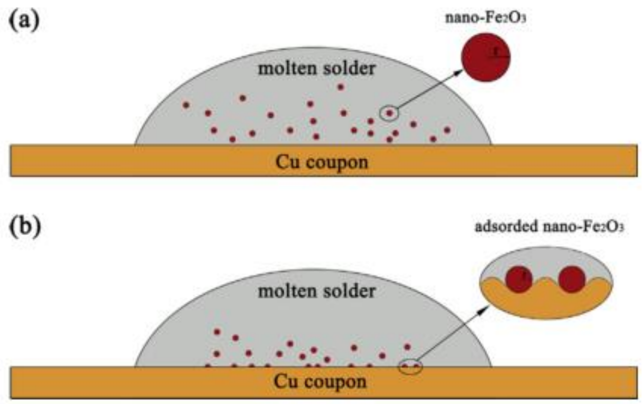


Figure 2.10 Schematic diagram showing nano composite-solder and Cu coupon system (a) before and (b) after nanoparticles adsorption [24]

Besides that, the effect of Fe2o3 in microstructure of solder joint is studied. By adding the Fe_2O_3, the shape of IMC layer has changed from elongated scallop to round scallop shape which results in stronger solder joint. When small size of nanoparticles of Fe_2O_3 added into the solder, it cause refinement of beta-Sn grains in solder matrix. This is because nanoparticle surround the Sn grain boundary and produced great pinning force on the grain boundary and act as diffusion barrier to inhibit grain growth of beta-Sn. The smaller that size, the larger the restraining force and smaller the grain size.[25] Thus, load-dependent hardness of composite solder is increase with the addition of percentage of Fe_2O_3.[26]

2.6 Reinforcement of NiO in nanocomposite solder

There are few research focus on study the addition of NiO in solder paste on mechanical properties of solder joint. From research of S.Chellvarajoo, melting temperature of composite solder is increase with addition of NiO. High-percentage of NiO nanoparticle reinforcement elicited an alloying effect on Pb-free solder paste, which needs additional thermal energy to achieve the molten state. Besides that, the thickness of the IMC layer is decrease and hardness of composite solder increase with addition of NiO. Both properties is due to pinning mechanism of nanoparticle of NiO at grain boundary as discussed in TiO_2. High impede to dislocation of grain boundary leads to increase of hardness of composite solder. The displacement of Nio nanoparticle move from composite matrix and precipitate on surface of Cu6Sn5 act as barrier to inhibit the growth of IMC layer. [28]

2.7 Summary

In this chapter, a full review on nanoindentation of the lead-free solder joint is done. Microstructure and mechanical behavior of IMC layer and tin-rich solder are studied by researchers to investigate the effect of different sample preparation parameters in the strength of solder joint. In nanoindentation experiment, different parameters are associated with creep effect in the sample which also leads to strain-hardening of the sample surface.

Besides that, researches on nanoparticle reinforced solder with mechanical characteristic changes state that different concentration of nanoparticles reinforcement affects differently on the structure of solder joint. As nanoparticle embedded in the solder paste, it diffuses with the intermetallic compound in nanocomposite solder to prevent the agglomeration of IMC. The refinement of IMC is then adsorbed on the surface of IMC layer between IMC/Cu boundary, impede the diffusion of copper atom into tin-rich solder and thus the thickness of IMC layer is retained. Refinement of IMC in nanocomposite solder allows small IMC pinned in tin-rich solder to prevent dislocation of solder. Thus, the hardness of nano-reinforced solder is higher than pure solder. However, the effect is deteriorated when the concentration of nanoparticle has exceeded the limit. The IMC in nanocomposite solder will entangle with each other to form a large compound. Therefore, the mechanical properties are changed.

Chapter 3 Methodology

3.0 Overview

In this research, the methodology was separated in 2 sections which are sample preparation and characteristic of lead-free solder joint inspection. The process flow in sample preparation is listed as in Fig.3.1. There are 4 types of samples are used in this research as scope of interest which are pure 305 SAC, 305 SAC + xTiO_2 , 305 SAC + xFe_2O_3 and 305 SAC + xNiO. After samples preparation, characteristic of solder joint is inspected as process in Fig.3.10. In indentation process, experiment parameters were tried to obtain optimum setting of experiment. Then, the inspection proceed and all the results were recorded.

3.1.0 Preparation of Surface-Mounted Packages Sample

The ultra-fine packages used is 01005 capacitor with dimensions of 0.4mm x 0.2mm. For nano-reinforced lead-free solder, nominal percentages of 0.05 wt%TiO_2, Fe_2O_3 and NiO nanoparticles were mixed with 96.5 Sn-3.0Ag-0.5Cu solder paste. Solder paste mixing process was ignored for 305 SAC due to free from nanoparticles reinforcement. 305 SAC was proceeded to solder paste printing step. Then, the process was followed as Fig 3.1.

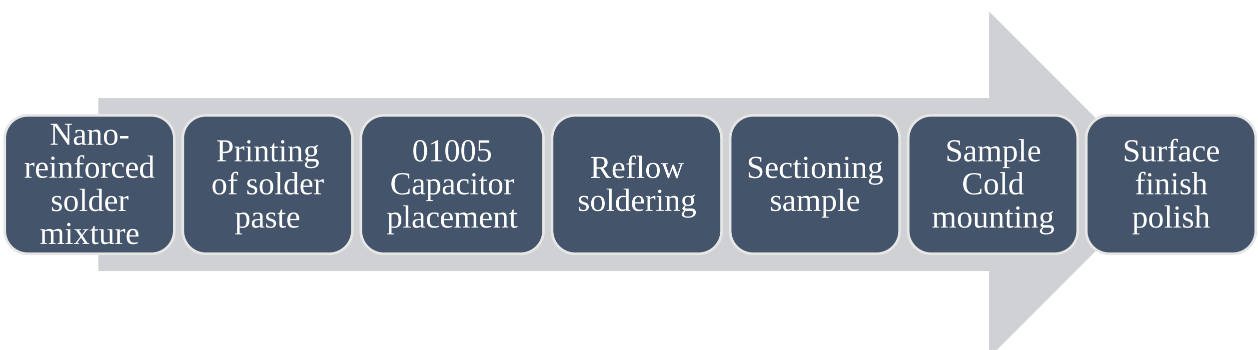


Figure 3.1 Process flow of sample preparation

3.1.1 Mixing of Nanoparticles and Solder Paste

The nanoparticle mixed with 305 SAC by using a mechanical stirrer (Fritsch Planetary Mill PULVERISETTE 5) for 15 mins with 300 rpm to ensure the nanoparticles are distributed evenly in solder paste.

3.1.2 Printing of Nanocomposite Solder Paste

The nano-reinforced lead-free solder paste printed on PCB with thickness of approximately 0.13mm using a laser cut-stainless steel stencil (nano-coated with 1:1 aperture – 0.2 x 0.2mm) and a steel squeegee.

3.1.3 Placement of Capacitor on PCB

The 01005 capacitors were automatic mounted onto the specific printed solder paste by using automated robotic FUJI NXT (FUJI Scalable Placement Platform NXT III) equipment. The head of the machine was changed. 01005 capacitors were placed in feeder station. Then capacitor were picked and placed on the solder paste on PCB automatically.

3.1.4 Reflow Soldering

A full convection reflow oven (Vitronics Soltec XPM2) was used to execute the reflow soldering process with a lead-free reflow profile under a nitrogen-filled environment. The reflow soldering process included 3 stages: preheating, reflowing and cooling. The reflow temperature profile for reflow soldering process is shown in Fig.3.2 with a peak temperature of 239.73ºC.

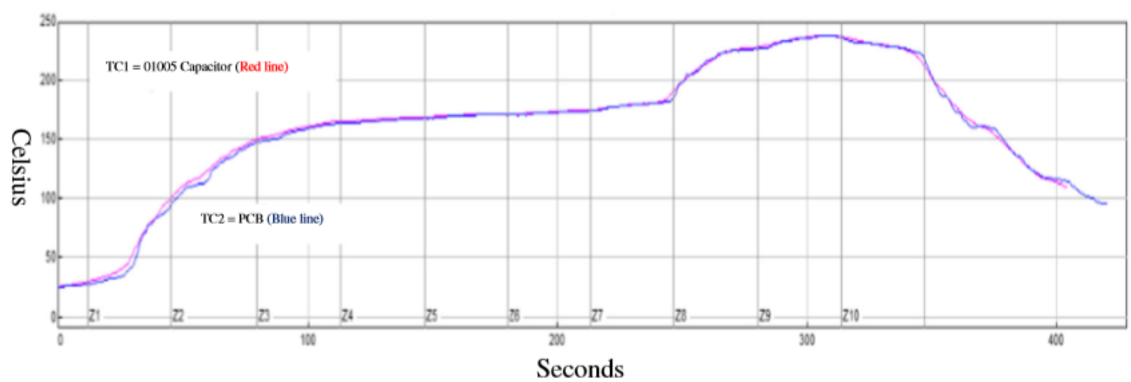


Figure 3.2 Mass reflow temperature profile for the reflow ultra-fine package

3.1.5 Sectioning Cut of Sample

Figure 3.3 Medium Duty Abrasive Cutting Machine META-CUT-1E

The abrasive cutoff disk used in abrasive cutting machine as shown in Fig.3.3 is diamond saw. The PCB was clamped at the workplace in cutting machine. Then, the cover was closed then machine was turned on and the movement of diamond saw was controlled manually to cut the PCB.

3.1.6 Cold Mounting of Sample

a b

Figure 3.4 a) Epoxy, hardener resin and mold releasing agent b) Mold cup with mixture resin and sectioned sample

One layer of mold release agent as shown in Fig 3.4a was applied onto the mold cup surface and dried. The sectioned sample was placed between mounting ring perpendicular to the base using sample support clips. The surface to be examined was faced downward. The ratio of mixing is epoxy resin 10g to Hardener resin 2g. (Epoxy: Hardener = 5:1). The mixture of resin was stirred by using stirring rod in same direction for 1 minutes. Then the resin was placed inside vacuum chamber to release the trapped gas for several time. The mixture resin was pour slowly into mold cup as in Fig 3.4b. The cold mounted sample was take out from mold cup after it is harden.

3.1.7 Sample Surface Polishing

The samples are required to do 2 surface polishing processes which are rough polish and fine polish to remove surface dirt and reduce irregularities of the surface due to oxidation and moisture of sample surface. This is to increase accuracy of hardness and reduced modulus measurement of nanoindentation. Surface of sample was observed under microscope before surface polishing to compare the different after polished.

Figure 3.5 OLYMPUS BH2-UMA

The samples was put at the workplace table of the OLYMPUS microscope as in Fig 3.5. The observation started with lowest focus power lens $\infty/-f = 180$ which is 0.10 to trace the area of interest of the sample. Then, magnificent lens were changed to 0.20 and at last to 0.25 for largest magnificent to observed the surface roughness of solder joint. Then, samples transferred to surface polisher station.

a b

Figure 3.6 Polish device a) Hand Grinder Manual Polisher b) KNUTH-Rotor 2 Rotary Grinder Polisher

For rough surface polishing, 5 different roughness of sandpapers were put into column of hand grinder as shown in Fig.3.6a. The grinding sequence of sample was started from high roughness to lowest which 220#, 800#, 1200#, 2400# and 4000#. The grinding process continued until flat surface was observed. Then, the sample were transferred to fine polishing which is 6-µm rotary grinder polisher as shown in Fig 3.6b. The 6-µm diamond paste was distributed evenly on polish cloth. The samples were polished for 30 minutes by using rotary polish grinder with constantly washed by pipe water. Then, 1- µm alumina powder was distributed on the polish cloth before polishing. The samples transferred to 1 - µm polish disk to polish for 30 minutes using rotary polish grinder with constantly washed by water pipe. Height of polished sample must not inclined to avoid difficulty in focus of microscope at nanoindentation process.

Figure 3.7 METASERV Sample Dryer

The samples were placed on the tray as shown in Fig 3.7 and dried by using sample dryer with heater for about 20 minutes and cooled down with blower only for 15 minutes. The sample was observed under microscope to ensure the surface was well-polished. Fig 3.9 is comparison of before and after fine polishing.

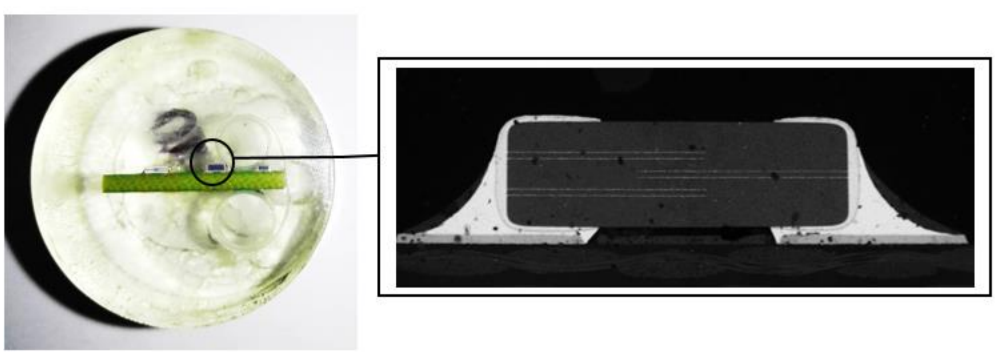


Figure 3.8 Mounted sample in cold epoxy and SEM image of solder joint

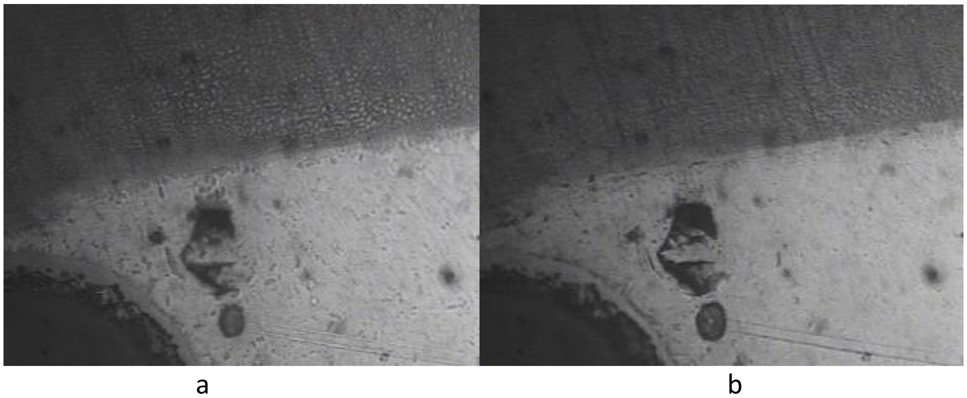


Figure 3.9 Optical Microscope image a) before and b) after polish

3.2.0 Mechanical Characteristic Testing of Solder Joint

In mechanical characteristic testing section, samples done on 4 processes as in Fig 3.10. The nanoindentation experiment done to extract data of hardness and elastic modulus of samples. Then, the sample passed to thin film coating before observed under scanning electron microscope. At the end, 3D-high resolution surface profile imaging was done to visualize the surface roughness of samples.

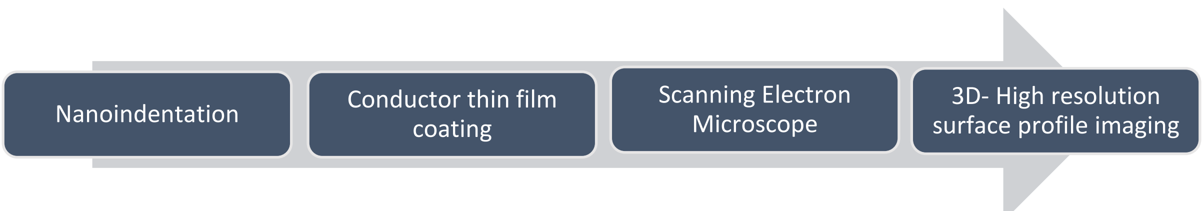


Figure 3.10 Process flow of investigation of mechanical characteristic testing of solder joint

3.2.1 Nanoindentation testing

The thickness of intermetallic compound layer in solder joint of sample is averagely around 2-7 µm. Therefore, Micro Materials NanoTest Vantages with Berkovich indenter was used to measure hardness and reduced modulus of solder joint in this research.

Figure 3.11 Micro Materials NanoTest Vantage