Solid state interfacial reaction of Sn-3.5Ag solders with Ni-P and Ni-W-P under bump metallization

Zhang, Keran

2016

Zhang, K. (2016). Solid state interfacial reaction of Sn-3.5Ag solders with Ni-P and Ni-W-P under bump metallization. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/68911>

<https://doi.org/10.32657/10356/68911>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**SOLID STATE INTERFACIAL REACTION OF Sn-
3.5Ag SOLDERS WITH Ni-P AND Ni-W-P UNDER
BUMP METALLIZATION**

ZHANG KERAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

**SOLID STATE INTERFACIAL REACTION OF Sn-3.5Ag
SOLDERS WITH Ni-P AND Ni-W-P UNDER BUMP
METALLIZATION**

ZHANG KERAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2016

Abstract

(Ni-P and Ni-W-P) were developed as the soldering metallization in this work to solve the potential reliability. The interfacial reactions between lead-free Sn-3.5Ag solder and these ternary metallizations during reflow and thermal aging were investigated. The interfacial reaction between the same solder and electrolessly-plated binary Ni-P metallization was compared to understand the effect of the addition of the ternary element. Among all four types of metallizations, Ni-P is consumed at the fastest rate, while Ni-W-P is consumed at the slower rate.

During the Ni-P/Sn-3.5Ag interfacial reaction, as predicted based on the limited available information on the Ni-P phase diagram, the formation of Ni_3P is formed. Scattered cracking occurs in Ni_3P and Ni_3Sn_4 metallization layers. Though the overall consumption rate of the Ni-P metallization is slow, the presence of scattered cracking leads to fast degradation of the Ni-P/Sn-3.5Ag solder joint strength.

In the case of Ni-W-P, two IMCs, Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ are formed. No voids are found at the reaction interface after prolonged reaction. The amorphous nature of the $(\text{Ni,W})_3\text{P}$ layer makes it an effective diffusion barrier for Ni, resulting in the slowest thickness reduction for Ni-W-P metallization. The growths of both Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers are found to be diffusion-controlled. The activation energies for the growth of Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers during solid-state reaction are determined to be 62.3 kJ/mol and 58.2 kJ/mol, respectively.

Acknowledgments

I would like to take this opportunity to acknowledge the guidance, support, and assistance received during this work.

First of all, I sincerely express my great gratitude to my supervisor, A/P Huang Yizhong, for his invaluable guidance, advice, and encouragement throughout the course of this study. I would also like to thank Dr. J. N. Balaraju and Dr. K. Chen for their advices on electroless plating. Without their supervision and constant support, this work could not be accomplished.

I am thankful to all of my friends in the School of Materials Science and Engineering, Nanyang Technological University, for their friendship and inspiration. In particular, I thank Mr. Zhang Bowei for his help with SEM and TEM operation. I would like to thank Dr. Tay Yee Yan for his help with TEM sample preparation as well.

I express my deepest gratitude to my parents for their great love and support at every moment of my life.

Table of Contents

Abstract	i
Acknowledgment	iii
Table of Contents	v
Figure Captions	vii
Abbreviations	ix
Chapter 1 Introduction	1
1.1 Background and motivation.....	2
1.2 Objectives.....	6
Chapter 2 Literature Review	7
2.1 Pb-Free solder.....	7
2.2 Ni-Based Under Bump Metallization.....	8
2.3 Electroless Nickel Plating.....	9
2.4 Ni-P and Sn-bearing solders interfacial reaction.....	11
2.5. Morphology of Intermetallic Compound.....	16
2.6 Diffusion and Reaction Mechanism at the Ni-P/Solder Interface.....	17
2.7 Effect of Phosphorus on Element Diffusion in Ni-P System.....	21
2.8 Factors Causing the Brittle Failure of Ni-P/Solder joints.....	22
Chapter 3 Experimental Methodolog	25
3.1 SEM introduction and principle.....	26
3.2 TEM introduction and principle.....	28
Chapter 4 Results and Discussion	37
4.1 Ni/P- Sn3.5 Ag solder interfacial analysis by SEM.....	38
4.1.1. Crystallization Behavior of Electroless Ni-P.....	39
4.2 Ni/P- Sn3.5 Ag solder interfacial analysis by TEM.....	42
4.2.1. Transition of Ni ₃ Sn ₄ Morphology.....	47
4.2.2 Growth Mechanism of Interfacial Compounds.....	48

4.3 Ni/W/P- Sn3.5 Ag solder interfacial analysis.....	49
4.3.1 Result and discussion of Ni-W-P.....	49
4.4 Results and discussion of Ni-P and Ni-W-P.....	58
Chapter 5 Conclusions.....	61
Chapter 6 Future Work.....	63
References.....	65

Figure Captions

Figure 1.1 schematic illustration of the architecture of a typical flip chip.....	3
Figure 2.1 The equilibrium phase diagram of Ni-Sn binary alloy5.....	13
Figure 2.2 The equilibrium phase diagram of Ni-P binary alloy.....	14
Figure 2.3 Possible elemental diffusion mechanism in the interfacial reaction between electroless Ni-P and eutectic Sn-Pb solder.....	18
Figure 2.4 (a)plane-view of a Ni substrate with the deposited Ti (b) cross-sectional view of the Ni/Sn diffusion couple prior to aging, and (c) after aging at 225 ° C for 1000 h.....	19
Figure 2.5 Schematic illustration of the interfacial elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-3.5Ag interface.....	21
Figure 3.1 illustration of SEM machine.....	26
Figure 3.2 illustration of SEM working process.....	27
Figure 3.3 illustration of SEM machine.....	28
Figure 3.4 TEM working principle.....	29
Figure 3.5 difference of TEM and SEM.....	30
Figure 3.6 Schematic illustration of soldering joint.....	32
Figure 3.7 Diced bulk sample plate with a thickness (350 μm).....	33
Figure 3.8 3mm disc with a thickness of 100 μm	34
Figure 3.9 TEM sample after ion milling.....	35
Figure 4.1.1 Backscattered electron image (BEI) of the interfacial layer between Sn-3.5Ag solder and Ni-P as reflowed.....	38
Figure 4.1.2 SEM BEI of the interfacial layer between Sn-3.5Ag solder and Ni-P after aging at 180 °C for 100 h.....	39
Figure 4.1.3 SEM BEI f the interfacial layer between Sn-3.5Ag solder and Ni-P after aging at 180 °C for 300 h.....	40

Figure 4.1.4 SEM BEI of the interfacial layer between Sn-3.5Ag solder and Ni-P after aging at 180 °C for 1000 h.....	41
Figure 4.2.1 A bright field TEM image of the cross-section between the Ni/P substrate and the Sn3.5 Ag solder.....	42
Figure 4.2.2 A magnified HR-TEM image of square 1 in Fig. 4.2.1 and two FFT patterns on square A and B, respectively.....	43
Figure 4.2.3 A magnified HR-TEM image of square 2 in Fig. 4.2.1 and two FFT patterns on square C and D, respectively.....	44
Figure 4.2.4 STEM EDX mapping of the cross-section between NiP substrate and Sn3.5 Ag solder (a) STEM image, (b) Ni, (c) P, (d) Sn.....	46
Figure 4.3.1 EDX COMPOSITIONAL RESULT OF Ni-W-P layer.....	49
Figure 4.3.2 Backscattered electron image (BEI) of the interfacial layer between Sn-3.5Ag solder and Ni-W-P as reflowed.....	50
Figure 4.3.3 Backscattered electron image (BEI) of the interfacial layer between Sn-3.5Ag solder and Ni-P at 180 °C for 1000 h.....	51
Figure 4.3.4 A bright field TEM image of the cross-section between the Ni/W/P substrate and the Sn3.5 Ag solder.....	52
Figure 4.3.5 A magnified HR-TEM image of square 1 in Fig. 4.3.1 and three FFT patterns on square 1, 2 and 3, respectively.....	53
Figure 4.3.6 A magnified HR-TEM image of square 2 in Fig. 4.3.1 and three FFT patterns on square 1 and 2, respectively.....	54
Figure 4.3.7 A magnified HR-TEM image of square 3 in Fig. 4.3.1 and three FFT patterns on square 1 and 2, respectively.....	55
Figure 4.3.8 STEM EDX mapping of the cross-section between NiP substrate and Sn3.5 Ag solder (a) STEM image, (b) Ni, (c) P, (d) Sn.....	57

Abbreviations

AC	Alternating Current
BGA	Ball Grid Array
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive X-ray Spectroscopy
EMPA	Electron Probe Micro Analyzer
IC	Integrated Circuit
IMC	Intermetallic Compound
I/O	Input/Output
PCB	Printed Circuit Board
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

In this chapter, the basic concept of bonding and soldering in interconnect technologies will be introduced. Flip chip soldering technology which is used in this study will be explained more. Solder joint failure may occur when the thin UBM is fully consumed by soldering reaction. Therefore, slow IMC growth is needed to be beneficial for the solder joint reliability. The materials chosen for solder joint in this study are Ni-W-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag. Lastly the objectives will be made and list the works need to be done in this study.

1.1 Background and motivation

Recently bonding and soldering are widely used in interconnect technologies in the packaging industry. Between these two methods, soldering is an area array technology which could potentially provide higher input/output (I/O) density, as compared to wire bonding, which is only used in peripheral joining. For solder joint, it provides not only electrical but also thermal connection in an electronic device¹. According to this, its reliability is much more important due to its critical importance. Because the failure of a single solder joint will lead to the failure of the electronic device, sometime even the entire system. As the trend which electronics industry tends to increase higher I/O counts and smaller feature size, coupled with more strict restriction on materials toxicity (e.g. lead-free), the packaging industry faces ever greater challenges with regards to the interconnect reliability in the coming decades. As compared to other inventions, flip chip soldering technology has already been proven to be a promising technology to cope with these challenges.

Figure 1.1 schematic illustration of the architecture of a typical flip chip

Figure 1.1 shows an illustration of the architecture of a typical flip chip solder joint. In this flip chip joint, the region is in direct contact with the solder on the surface of the chip side is the Under Bump Metalization(UBM). The UBM consists of a series of thin metal layers, which are deposited on the integrated circuit. It also provides a good wetting surface. Similarly, the solder pad on the substrate side is called substrate metallization. During the reflow process and service, interfacial reactions occur between solder and the metallization on both Integrated Circuit and substrate. During the reflow process, the solder undergoes a temperature cycle which is above the solder melting temperature which causes liquid state reactions. This reaction proceeds very fast and its duration is short, i.e. around 60s. While during service, solid-state reactions occur at temperatures which is lower than the melting point of solder. Liquid-state reaction proceeds much faster than solid state reaction, but solid state reaction has a longer duration. In both liquid-state and solid-state reactions, Intermetallic compounds(IMCs) form and continue to grow at the solder/metallization interface. The formation of IMCs is reported to achieve good metallurgical bond, but the excessive growth of IMCs has the ability to

degrade the mechanical reliability of the solder joint. Since UBM is typically very thin ($\sim 1 \mu\text{m}$), solder joint failure may occur when the thin UBM is fully consumed by soldering reaction. Therefore, slow IMC growth is needed to be beneficial for the solder joint reliability.

Among different metals, copper was once the most popular choice for the surface layer of UBM. The main reason is due to its good wetting behavior with solders, but it has a poor behavior when reaction with eutectic Sn-Pb solder. It was reported to be rapid and severe spalling of Cu-Sn IMCs was founded. In order to solve this problem, graded Cu/Cr was adopted by IBM while other strategies were also taken by other companies. However, with the trend to implement lead-free solders since July 1st 2006, new challenges regarding the reliability of solder joints were encountered, as commonly used lead-free solders react much faster with UBM than eutectic Sn-Pb solder. This is due to lead-free solders that mainly consist of Sn (typically $> 95 \text{ wt. } \%$), and have higher melting temperatures. In this case, Cu will be completely consumed by lead-free solders very fast. In the end, only IMCs appear at the interface resulting in the degradation of mechanical strength of the solder joint. This suggests lead-free soldering with Cu-based metallization may lead to some reliability concerns.

Lots of research effort has been done to slower the interfacial reaction to maintain the good wetting between solder and the metallization [1,2,10]. One approach is to change composition of solder by adding different elements into the solder alloys. However, this approach is applicable only to solders in paste form and may sometimes lead to many more different complicated interfacial reactions. The other approach is to change the metallization composition. After a few years, Ni and Ni alloys were found to possess a much slower reaction rate with Sn as compared with Cu and Cu alloys [1]. Ni-based metallization has received great attention in the lead-free area. Depending on the deposition techniques, there are several types of

Ni-based metallizations, including electrolytic nickel, sputtered nickel and electroless nickel. Among all of them, electroless nickel, which is a Ni-P alloy, has been extensively studied and widely used in many applications. It is produced by a mask-less selective process and has an excellent uniformity low residual stress and good solderability as well as low processing cost. Electroless plating is carried out in an aqueous solution which contains metal ions, complexing agents including a reducing agent and stabilizers.

1.2 Objectives

This research work mainly reports an experimental of the effects of the interfacial reactions on Cu/Ni-P/Sn-3.5Ag solder joint and Cu/Ni-W-P/Sn-3.5Ag. Electrical study aims at a systematic and comprehensive understanding of the solid-solid interaction of different UBM/solder systems stressed with high-density electric current. Moreover, an effort will be made to understand the effect of high-density electric current on the mechanical properties of different UBM/solder systems. Such understanding would provide guidance to the selection of working conditions as well as the materials of electronic packages in order to produce better and reliable products. The work covers several separate but inter-related sub-topics, as detailed below.

Chapter 2

Literature Review

In microelectronic packaging, solder joints are known to be one of the weakest links in electronic products. The reliability of a single joint could determine the service life and function of an entire electronic device. Hence, the study of interfacial reactions of solder joints is very important for reliability of electronic products. The present work mainly investigates the effects of interfacial reactions. This chapter reviews the literatures on the interfacial reactions between electroless Ni-P and Sn-bearing solder, mechanical properties of solder joint, electromigration phenomenon, and electromigration effect on solder joint.

2.1 Pb-Free solder

SnPb solder is widely used in nowadays electronic industry. Although Pb-free solder application has a great advantage in legislation and commercial cost, it still has an important environment-friendly electronics issues. Most of the Pb-free solders are basically Sn-based eutectic alloys, such as Sn and noble metals. Eutectic alloy is chosen mainly because it has not only single but also low melting point, thus the entire solder will melt and solidify at one temperature. Eutectic Sn noble metal alloy solder has higher melting point than SnPb solder, thus the reflow temperature for Sn-noble metals solder is higher than SnPb solder accordingly. In this case, it could increase the solubility and dissolution rate of UBM materials.

Most common type of Sn-based Pb-free solder is Sn-3.5Ag solder which has the melting point of 220°C. Problem arises when it reflows with electroless NiP UBM to form the solder joint in electronic packaging. The main problem is when it reflows with electroless Ni-P UBM to form the solder joint in electronic packaging. Electroless Ni-P has been reported to be consumed more rapidly when it reacts with the Sn-Ag solder compared to Sn-Pb solder. Even though the crystallization of Ni-P layer happens in both systems during the reflow soldering above 240°C, Ni-Sn IMC has a higher growth rate in electroless Ni-P/Sn-Ag solder interface than in electroless Ni-P/Sn-Pb solder interface [2]. Thus, the lead-free solders have a high risk of fast intermetallic growth which might affect the solder joint reliability significantly. Therefore, in lead-free solder applications, the reliability concerns are focused on how to slow down the intermetallic growth by designing a proper UBM alloy/solder system. While there are many investigations have been carried out on solder materials, this project will focus more on the materials for UBM application.

2.2 Ni-Based Under Bump Metallization

In IC packaging, under bump metallization (UBM) is usually a compatible and adhesion layer to promote a good interface between the solder bumps and final chip metallization. The mechanism is that it provides a consumable layer for solder to wet resulting in the formation of interfacial layers such as intermetallic compounds (IMC). However, the excess growth of IMC can bring about local embrittlement and thermal expansion leading to the degradation of the mechanical strength.

The Cu-based UBM is widely used due to its high conductivity. However, it faces the problem of CuSn IMC spallation and rapid consumption of Cu UBM due to the fast reaction between solder and Cu-based UBM. Ni-based UBM has been chosen as the preferred UBM over Cu due to its slow wetting reaction with Sn-based solder compared to Cu-based UBM. The IMC at the interface between Ni-based UBM and solder was reported to have slower growth rate compare to the IMC at Cu-based UBM and solder interface. Therefore, the present work will focus on the Ni-based UBM.

2.3 Electroless Nickel Plating

Among all types of Ni-based metallization (sputtered nickel, electrolytic nickel and electroless Ni-P), electroless Ni-P is reported to have widely adopted in many applications. It has several advantages i.e. the lowest manufacturing cost and lower residual intrinsic stress than sputtered nickel. Besides, since both electroless and electrolytic platings are based on aqueous reactions, electroless Ni-P is far superior to electrolytic nickel for coating application. In addition, electroless Ni-P more uniform surface finish than electrolytic nickel. It has a large flexibility of thickness and volume on the surfaces of metal, so that it can easily fill recesses or pits in the metal surface. Electrolytic plating process requires complex filtration equipment and an external electrical source, while electroless plating process is an autocatalytic chemical reduction

which requires no extra equipment. Corrosion resistance of electroless Ni-P is much higher than electrolytic nickel. This is because electroless Ni-P is normally an amorphous glass-like nickel phosphorous alloy and has better thickness distribution than electrolytic nickel.

In the case of electroless nickel plating, reduction of Ni^{2+} ions from an ionic Ni solution occurs in the presence of a hypophosphite (H_2PO_2^-) reducing agent. The reactions occur during electroless nickel plating are listed below:

The standard electrode potential (E_o) for the reduction reaction is -25 mV, while the E_o for the oxidation reaction is +50 mV, so the E_o for the overall reaction is +25 mV. However, Reaction 1.3 does not represent the true electroless Ni plating reaction since hydrogen gas is also generated during the plating process.

The physical and chemical properties of electroless Ni-P is depended by the composition and operating conditions of the plating solution. Typically, an electroless nickel plating solution contains a source of a reducing agent, nickel ions, complexing agents and stabilizers. In general, nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) is the preferred nickel source. Sodium hypophosphite has been used most which is because sodium hypophosphite is most commonly available and has low cost, good stability and ease of preparation. Complexing agents have several advantages. First, they can prevent the nickel salts from precipitation, such as basic salts or phosphites. Second, they can impede the fast decrease of the pH of the electroless nickel plating solution. Third, they can reduce the concentration of free nickel ions in the plating solution. The typical choice for

complexing agents is either lactic acid ($\text{C}_3\text{H}_6\text{O}_3$), ammonium ion (NH_4^+) or citrate ion ($\text{C}_6\text{H}_5\text{O}_7^{3-}$). In real practice, more than one complexing agents can be used to optimize the plating process. During electroless nickel plating process, an increase in the volume of the generated hydrogen gas and the presence of a black precipitate in the solution may lead to spontaneous decomposition of the plating solution. The black precipitate normally consists of nickel particles, and either nickel phosphide or nickel boride, which depends on the type of the employed reducing agent. Trace stabilizers is used to prevent such decomposition of the plating solution. The choices for stabilizers are compounds of group VI elements (S, Se and Te), heavy metal cations (Sn^{2+} , Hg^+ , Pb^{2+} and Sb^{3+}), compounds containing oxygen (AsO_2^- , IO_3^- and MoO_4^{2-}), and unsaturated organic acids (maleic and itaconic).

Besides the formulation plating solution, operating conditions also affect the properties of electroless Ni-P. The operating conditions of electroless nickel plating are controlled by process parameters, such as plating temperature and pH of the plating solution. With increasing the plating temperature, the electroless deposition rate increases due to the general endothermic nature of the deposition reaction. However, there is an upper limit for the plating temperature of electroless Ni-P since the plating solution may decompose at a temperature beyond 100°C . With increasing the pH of the plating solution, the deposition rate increases due to accelerated reduction of nickel ions [4]. However, decomposition of the plating solution may happen when the reduction of nickel ions is too fast. Although lowering the pH of the plating solution can enhance the buffering action to prevent the decomposition, there is still a lower limit for the pH value since the deposition reaction will be retarded when the pH is too low.

2.4 Ni-P and Sn-bearing solders interfacial reaction.

The interfacial reactions take place during both reflow soldering process and service. Both types of reactions result in the nucleation and growth of IMCs at the

metallization/solder interface. Since Ni-based metallizations have a much lower reaction rate with Sn-bearing solders in comparison with Cu-based metallizations, extensive studies on Ni-based metallizations have been conducted over the past two decades. There are several types of Ni-based metallizations, such as sputtered nickel, electrolytic nickel, and electroless nickel. Among them, electroless NiP is reported to be mostly used as metallization for solder joint. Electroless Ni-P plating is carried out through autocatalytic chemical reduction of nickel ions. Unlike electroplating, electroless plating process does not require electrical source, so the coatings on non-conductive substrates can be achieved by this method. Moreover, another advantage of electroless plating is its ability to deposit the alloy coating uniformly on an irregular surface.

From the equilibrium phase diagram of Ni-Sn binary alloy (Fig. 2.1), it will be much easier to tell possible IMC compounds those may form during interfacial reaction. Between certain types of Ni-based metallization to the IMC phases that can be possibly formed during interfacial reaction between certain type of Ni-based metallization and the solder with a known composition under reflow and/or service condition can be listed. According to this phase diagram, three types of IMCs can be formed between Ni and Sn, which are Ni_3Sn_4 , Ni_3Sn_2 and Ni_3Sn [5]. Among these IMCs, Ni_3Sn_4 was reported to be the primary IMC formed by the interfacial reaction and various Sn-bearing solders during normal reflow process in a temperature range of 200-260°C. Besides this predominant Ni_3Sn_4 layer, the formation of other Ni-Sn compounds, Ni_3Sn_4 and $\text{Ni}_{48}\text{Sn}_{52}$ was reported as well. However, both compounds were found to have a submicron thickness, which makes them difficult to be observed under SEM or even under TEM. The small thickness of these compounds may be attributed to their slow nucleation and/or growth.

Figure 2. 1 The equilibrium phase diagram of Ni-Sn binary alloy[10][11].

During electroless nickel plating, reduction of Ni^{2+} ions occurs in the presence of a hypophosphite (H_2PO_2^-) reducing agent. Thus, the P content in electroless Ni-P coating cannot be avoided since it comes from the hypophosphite reducing agent. However, the presence of P not only influences the microstructure of Ni-P. The complication of soldering reaction with Ni-P is because it results in the formation of both Ni-Sn and Ni-P compounds while soldering reaction with pure Ni results in the formation of Ni-Sn compound alone. From past studies, electroless Ni-P is reported to have a microcrystalline structure when it contains less than 12.5 at.% of P, while it has an amorphous structure when its P content is higher. The electroless Ni-P used as metallization in electronic packaging normally has an amorphous structure since it contains more than 12.5 at.% of P. The crystallization of such amorphous Ni-P alloy can take place spontaneously during thermal treatment at a temperature when crystallization occurs [6]. From Figure 2.2, the phases to be formed through the crystallization of

electroless Ni-P can be predicted. According to this phase diagram, Ni and Ni₃P are the thermodynamics equilibrium phases that are present close to the composition of electroless Ni-P. In addition, that microstructure of amorphous electroless Ni-P changes into a fine crystalline structure during self-crystallization process.

Figure 2. 2 The equilibrium phase diagram of Ni-P binary alloy[10][11].

When electroless Ni-P reacts with Sn-based solder, the amorphous Ni-P will be triggered at reflow temperature (200-260°C) that is below the self-crystallization temperature of Ni-P (350°C). Which will form Ni₃P from Ni-P. This Ni₃P layer was reported to have a fine columnar structure. Although Ni₃P is widely reported to be the primary phase, other Ni-P phases have also been found in the crystallized Ni-P layer. For example, Liu et al.

has reported the formation of two separate layers of Ni_3P and Ni_{12}P_5 in electroless Ni-P/Sn-Pb solder joint after aging at 150 ° for 30 days. Besides, Sohn et al. has studied the interfacial reaction in the high P concentration (9 wt.%) electroless NiP/Sn-3.5Ag solder joint after 30 min of reflow at 250 °C. In early report, which has summarized the differences between the two types of crystallization of electroless Ni-P with 12-19 at% of P (common composition of Ni-P alloys used as UBM). First, these two types of crystallized Ni-P have different compositions. The final products of the self-crystallization of Ni-P during thermal annealing were reported to be Ni_3P and Ni, while the product of the solder reaction-assisted crystallization is either a single Ni_3P phase or a mixture of Ni_3P phase and other Ni-P phases with a lower Ni to P ratio than that in Ni_3P . This can be explained that, during soldering reaction, Ni atoms diffuse out of the electroless Ni-P layer to react with the Sn atoms from the solder forming Ni_3Sn_4 compound. The two types of crystallized Ni-P have quite different microstructures. The solder reaction-assisted crystallized Ni-P was reported to have a well-developed fine columnar structure, while the self-crystallized Ni-P has coherent precipitates, which are observed as small evenly distributed dark particles. Besides Ni-Sn and Ni-P compounds, a ternary Ni-Sn-P compound was also found to present between the Ni-Sn and Ni-P compounds. The thin layer of Ni-Sn-P compound with a few hundred nano-meter thickness was found to consist of Ni_2SnP phase or Ni_3SnP phase by using TEM, while the thick layer of Ni-Sn-P compound with a few micron thickness was identified to be Ni_2SnP phase by using electron probe micro analyzer (EPMA) and SEM[6][7]. In recent years, Duh et al. has studied the relationship between the formation of Ni_2SnP and the evolution of P-rich layer (Ni_3P , or Ni_{12}P_5 , or Ni_2P layers) [8]. They found that in the Ni-13wt.% P/Sn-3.0Ag-0.5Cu solder joints after three reflows, the P-rich layer would transform to some layer compounds, including Ni_3P , Ni_{12}P_5 and Ni_2P , probably influenced by the formation of Ni_2SnP phase. According to the Ni-P phase diagram (Fig. 2.2), it is understood that Ni_3P , Ni_5P_2 and Ni_{12}P_5 are all thermodynamically stable. Based

on a continuously varied composition profile, following the Ni_3P phase, the next phase likely to be formed is Ni_5P_2 , since it is the second P-rich phase. However, it was reported that with further reaction at the Ni-13wt.% P/Sn-3.0Ag-0.5Cu interface, Ni_3P would transform to Ni_{12}P_5 , which is the third P-rich phase in the Ni-P phase diagram. In such event, the formation of Ni_5P_2 was hindered.

2.5. Morphology of Intermetallic Compound

The formation of IMCs at the solder/UBM interface can be attributed to a surface reaction occurring between solder and UBM. Both liquid-state and solid-state reactions lead to the change in morphology of intermetallic compounds. Other than state of reactions, there are several materials and processing factors that affect the morphology of intermetallic compounds. Material factors are the quantity of solute in Sn-matrix and the microstructure of solder and UBM. Processing factors are the reflow parameters such as the peak temperature, the dwell time over melting temperature of solder and the post-reflow cooling rate [9].

Ni_3Sn_4 IMC with two types of morphologies, needle-type and chunky-type form at the electroless Ni-P/solder interface during reflow. At the beginning of reflow, the formation of needle-type Ni_3Sn_4 grains dominates. Chunky-type Ni_3Sn_4 grains form and grow at the expense of needle-type Ni_3Sn_4 grains when the reflow time is prolonged. At the meantime, variation of the P concentration of electroless Ni-P layer does not affect the morphology of Ni_3Sn_4 grown at the interface.

There are a few studies in which the morphology of intermetallics is also affected in terms of size as well as shape by cooling rate. However, most of these studies focus on the change of IMC morphology in bulk solder rather than at solder/UBM interface.

The effect of cooling rate on IMC morphology is reported more important in the present of electroless Ni-P UBM than that of pure Ni.

In solid-state reactions, the morphology of Ni_3Sn_4 becomes quite different as compared to liquid-state reactions. A continuous layer of Ni_3Sn_4 IMC with curved chunky-type or more appropriately scallop-type morphology has been reported to form during solid-state reaction instead of needle-type and chunky-type grains with channels that formed in the case of liquid-state reflow [9].

2.6 Diffusion and Reaction Mechanism at the Ni-P/Solder Interface

During soldering reaction, the formation and growth of a single compound is quite complicated since it involves several interfacial processes such as elemental dissolution in solder, elemental diffusion, phase nucleation, and creation and/or annihilation of defects. Since multiple compounds form in an electroless Ni-P/solder system, the interfacial elemental diffusion and reaction mechanism in this system becomes even more complicated.

In order to understand the interfacial elemental diffusion and reaction mechanism in electroless Ni-P/solder systems, there is a need to find out the dominant diffusing species first. From the review of the previous studies, different elements, such as Ni or Sn or P, have been considered to be the dominant diffusing species. Jang et al. have proposed two possibilities of elemental diffusion mechanism in the interfacial reaction between electroless Ni-P and eutectic Sn-Pb solder. As shown in Fig. 2.3, one possible mechanism is Ni atoms diffuse out of the electroless Ni-P layer and move through the grain boundaries of the Ni_3P layer to reach the $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$ interface[10]. The other possibility is the Ni_3P compound decomposes into P and Ni at the $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$ interface, then P atoms move back by interstitial diffusion to the $\text{Ni}_3\text{P}/\text{electroless Ni-P}$ interface to grow Ni_3P layer. Based on their microstructural observation, no voids were found in the Ni_3P layer, so there is no convincing evidence for the former mechanism because the grain boundary diffusion of Ni atoms has to be accompanied with the back diffusion of vacancies [12]. Thus, they proposed the mechanism of Ni_3P dissociation and

re-formation. However, subsequent results from other studies supported the Ni out-diffusion mechanism. Ahat et al. reported the diffusion of Ni from the electroless Ni-P to the solder at the SnAgCu/Ni-P/Cu joint. Besides this, He et al. found voids in the Ni_3P layer at both of the electroless Ni-P/Sn-3.5Ag interface and the electroless Ni-P/Sn-Pb interface after prolonged aging at 150 °C, so they concluded that Ni is the main diffusing element in the Ni_3P layer[6].

Figure 2. 3 Possible elemental diffusion mechanism in the interfacial reaction between electroless Ni-P and eutectic Sn-Pb solder[10].

Moreover, in order to verify the dominant diffusing species in Ni_3Sn_4 , several marker experiments were performed. Lee and Lin(1994) used W marker in the electroless Ni-P/Sn-Pb solder joint, and their study concluded that Sn is the predominant diffusing species that reaches the Ni-P layer, while Ni remains in the Ni-P layer or diffuses slowly relative to Sn. Following on this study, a Ni-Sn diffusion couple with the patterned Ti stripes as marker was designed, as shown in Fig. 2.4. In this study, according to the location of the Ti stripes after aging, Sn was proven to be the dominant diffusing species in Ni_3Sn_4 .

Figure 2. 4 (a) plane-view of a Ni substrate with the deposited Ti (b) cross-sectional view of the Ni/Sn diffusion couple prior to aging, and (c) after aging at 225 ° C for 1000 h[10][11].

Based on all of these aforementioned studies, a partial but common understanding of elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-bearing solders

can be made, and elaborated as follows. Firstly, the growth of IMC requires not only Ni atoms from the electroless Ni-P layer but also Sn atoms from the solder [11]. Secondly, P atoms remain in the Ni-P layer, rather than participating in the elemental diffusion. Thirdly, a Ni_3P layer which contains higher P content than Ni-P forms in between IMC and the remaining Ni-P layer. Recently, the full understanding of elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-3.5Ag interface was reported by Kumar and Chen. As depicted in Fig. 2.5, three interfacial IMC layers, Ni_3Sn_4 , Ni_3P and Ni_2SnP , were found to form by the electroless Ni-P/Sn-3.5Ag interfacial reaction from their study. The Sn atoms diffuse out from the solder, first reach the solder/Ni-P interface to react with Ni atoms from the deposited Ni-P layer to form the Ni_3Sn_4 layer. The depletion of Ni from the Ni-P layer to form Ni_3Sn_4 leads to the formation of the Ni_3P layer within the Ni-P layer adjacent to the original Ni-P/ Ni_3Sn_4 interface. The formation of the crystalline Ni_3P follows the mechanism of solder reaction-assisted crystallization as explained before. Meanwhile, some Sn atoms from solder reach the Ni_3P / Ni_3Sn_4 interface, and react with Ni_3P to form Ni_2SnP . Moreover, the interdependent growth mechanisms and the related growth kinetics of these IMCs were revealed by Kumar and Chen[12][13]. They found that Ni_3Sn_4 and Ni_3P layers grow predominantly when the deposited Ni-P layer is not fully consumed. This is because at the beginning of reaction, most of the Sn atoms from the solder are consumed by the reaction with Ni atoms to form Ni_3Sn_4 , and only a small part of Sn atoms are consumed by the reaction with already-formed Ni_3P to form Ni_2SnP . However, when the deposited Ni-P layer is fully transformed into Ni_3P , leading to the termination of Ni supply, all Sn atoms can only react with the already-formed Ni_3P to form Ni_2SnP , so Ni_2SnP layer grows rapidly at this stage. Kumar and Chen also found that the growth of the Ni_2SnP layer is controlled by diffusion initially, but once the coated Ni-P layer is completely consumed, the growth of this layer is controlled by the reaction rate. In addition, voids were found in the Ni_3P layer, and the formation mechanism of such voids will be discussed in the following section [1] [2] [6].

Figure 2. 5 Schematic illustration of the interfacial elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-3.5Ag interface[12][13].

2.7 Effect of Phosphorus on Element Diffusion in Ni-P System

P atoms are retained by the interface between Ni-P and the layers. The diffusion processes of these two elements make the interface of and layer move toward original Ni-P layer. The formation of extra interfacial layers, such as Ni-Sn-P, or other Ni-P compounds between and Ni-P, makes the element diffusion very complicated. Some researchers studied the reaction and element diffusion process accompanied by crystallization of Ni-P in solder/Ni-P system, but the reported results do not agree with each other. There were no Kirkendall voids could be observed in their results. This fits well with the thickness growth of layer, which was observed to increase with annealing time. The report also suggested that P controls the diffusion process and is decomposed at the front interface and other researchers claimed that Sn was the major diffusion element. According to Liu and Shang [14], the formation of two new IMC phases, was the result

of reaction between Sn and P after annealing, because Sn diffuses is much faster than Ni [14]. There is one uncertain factor here that Sn reacts with P instead of Ni. If the reaction between Sn and P is true, it should happen at the beginning of solid state reaction. Yet there is no reported evidence probably either because the claim is not true, or because it is difficult to observe such thin layers. Some other researchers described Ni as the primary diffusion element. It is very hard for element to diffuse through because of lacking grain boundaries. Downside Ni could not compensate the consumption of Ni in the upper part of Ni-P. If voids formed in Ni-P layer, it should distribute not only at the interface of Ni-P and Cu but also other part of Ni-P layer. None of the existing work presents well the element diffusion process of solder/Ni-P UBM system in solid state reaction. As a matter of fact, the diffusion of elements is an inter-diffusion process and all of the element such as Ni, Sn and P in solder/Ni-P system should be considered. Detailed analysis will be carried out by in the current work.

2.8 Factors Causing the Brittle Failure of Ni-P/Solder joints

In general, the mechanical behavior of solder joint can be affected by several factors such as reflow and service temperatures, reflow and service durations, and the microstructural and physical properties of solder and metallization materials. Though all these factors are different, each of these factors influences the microstructure and intrinsic stresses of solder joints and thereby changes their mechanical behavior.

The solder joint is actually comprised of solder, metallization layers, and IMCs that form between solder and metallization. The formation of IMCs in a solder joint is closely related to the reflow and service conditions such as temperature and duration. The physical properties of these IMCs differ a lot from those of solder and metallization materials. The IMCs are much harder compared to the solder and metallization materials and this indicates their high brittleness (Frear *et al.*, 1994; Mallory and Hajdu, 1990) [19]

[20]. The growth of IMCs can be beneficial or detrimental for the reliability of solder joint. Formation of a thin layer of IMCs during soldering is desirable and beneficial to achieve good metallurgical bond between solder and metallization. However, the excessive growth of IMCs can affect the mechanical reliability of solder joint as they are very brittle in nature and can act as initiation site for micro-cracks. In addition, the difference of density among the IMCs, metallization, and solder can cause the development of intrinsic stresses in the solder joint due to the excess growth of IMCs.

The microstructure of solder joint is also related to the process and service conditions such as temperature and time. However, the change in the micro-structure of solder and metallization with the process and service conditions depends upon solder and metallization materials itself. Thus, it is imperative to understand the evolution of the micro-structure (interfacial as well as bulk) of solder joint and its effect on the mechanical properties of the solder joint.

Chapter 3

Experimental Methodology

In this study, the most of the lab-work is done by microscopy which are SEM and TEM. SEM is carried out to find the morphology of IMCs in the Ni-P/Sn-3.5Ag and Ni-W-P/Sn-3.5Ag interface, while TEM is used to determine the structure and phases of IMCs in the Ni-P/Sn-3.5Ag and Ni-W-P/Sn-3.5Ag interface.

It mainly consists of two parts in this chapter. First is the introduction of SEM (Scanning Electron Microscope), followed by the SEM operation and principle. The TEM (Transmission Electron Microscope) introduction and principle will be explained afterward. The difference of SEM and TEM will be also discussed. Lastly, the preparation of the TEM sample will be explained with details.

3.1 SEM introduction and principle

Scanning electron microscope has been widely used in many areas nowadays to identify the sample's topography and composition. The electron beams Signals coming from the interaction between the atoms of the specimen and the electron can produce the images of the detecting specimen. The most advantage of SEM is due to its high resolution. It can achieve resolution to 1 nanometer. The first SEM machines is made by Manfred von Ardenne in 1937. It is a fundamental invention, which is the first microscope with a very high magnification. The SEM in this study is shown below.

Figure 3.1 illustration of SEM machine

SEM operation and principle

Figure 3. 2 illustration of SEM working process

For the electron gun, it is made of Tungsten filament cathode due to its highest melting point and low cost. It is electrically heated to emit electron beam which has energy 0.2keV to 40keV. Once the beam goes through first condenser lens and second condenser lens, its spot lowers down to 0.4nm to 5nm in diameter. After it goes through the deflection coils and final lens, it can scan the specimen over a rectangular area.

The electron beam will lose energy when it interacts with the specimen. During the interaction, there is energy exchange. Thus elastic scattering electrons, emission of secondary electrons by inelastic and emission of electromagnetic radiation are formed and will be detected by certain detectors. In this case, the image of specimen with high magnification can be identified.

3.2 TEM introduction and principle

Compare to SEM, TEM can achieve an even higher magnification and more details of a specimen. With the help of SEM, only the specimen's morphology is obtained, to identify the specimen's different phases, TEM is been used in this study. The electron beam transmits through the ultra-thin sample and interact with it. Several signals are increase in the interaction (X-rays, auger elctron, light), thus the image is formed.

The image is magnified and focused onto imaging devices such as fluorescent screen or to be detected by a sensor such as a CCD camera. The development of TEM is the consideration of quantum mechanical behavior of electron. Thus, a single column of atoms can be identified with the help of TEM. The first TEM machine was originally installed at IG Farben-Werke in 1939. The TEM machine which is used in this study is shown below.

Figure 3.3 illustration of SEM machine

TEM working principle

Figure 3.4 TEM working principle[20]

Firstly, the electron beam emitted from the electron source. When it goes through the condenser lens, it is focused into a small coherent beam. After it goes through the condenser aperture, only the electrons with lower angle exist. After the beam strikes the sample, the portion which is transmitted depending on the thickness and electron transparency strikes the specimen. This beam is focused by the objective to a charge coupled device. Optional objective apertures are to enhance the contrast; the image is obtained to identify the details of the sample. During the image, the darker phases represent the areas with less electrons are transmitted through while the lighter phases represent the areas with more electrons were transmitted through.

Compare with SEM and TEM

<u>Differences between SEM and TEM</u>	
TEM	SEM
Electron beam passes through thin sample.	Electron beam scans over surface of sample.
Specially prepared thin samples are supported on TEM grids.	Sample can be any thickness and is mounted on an aluminum stub.
Specimen stage halfway down column.	Specimen stage in the chamber at the bottom of the column.
Image shown on fluorescent screen.	Image shown on TV monitor.
Image is a two dimensional projection of the sample.	Image is of the surface of the sample

Figure 3.5 difference of TEM and SEM

For TEM, it is based on transmitted electrons while for SEM, it is based on scattered electron. TEM can identify a lot more characteristic about the internal composition like morphology and crytallization while SEM focus on the specimen's surface morphology. For the preparation part, TEM samples need to be much thinner than SEM samples. The images are obtained by fluorescent screens in TEM, while the images are obtained monitors.

TEM Sample preparation

Preparation of the Metallizations by Electroless Plating

For the metallization of Ni-P. The substrate is made of Cu plates (99.98 wt.%) which has a thickness of 6 mm. The Cu plates were firstly well-polished. The etching time is 30 seconds with 35 vol.% HNO_3 . The Cu surface was activated by ruthenium-based pre-initiator. Ni-P plating was conducted in hypophosphite bath with a temperature of 88 ± 2 °C, pH level of 5.3 and 30 minutes time.

For the metallization of Ni-W-P. The substrate Cu used is the same as Ni-P. And also undergoes an etching time of 30 second. But the electroless plating is different. While Ni-W-P was conducted in alkaline bath with a temperature of 83 ± 2 °C, pH level of 8.8 and 60 minutes.

Solder Joints Formation

Solder joint formation for both Ni-P/Sn-3.5Ag and Ni-W-P is combining electrolessly-coated Cu plates with lead-free Sn-3.5Ag. To join the Cu plates and Sn-3.5Ag, in this study, a no-clean paste flux was first applied on top of Cu. The paste must be thin enough to avoid the thickness change in the Cu substrate and remove the oxidation particles during the soldering. After that, the Sn-3.5Ag solder wires are put orderly on the Cu plate surface. The schematic arrangement of the coated Cu plates and solder wires used to form solder joints is shown in Fig. 3.6. As illustrated, the arrangement comprised of alumina spacers (around 650 μm thick), which were hired to maintain a fixed and uniform thickness. The reflow soldering was done in an IR reflow oven.

Fig. 3.6. Schematic illustration of joining the electrolessly-coated Cu plates.

In the present work, traditional method for TEM sample preparation has been used, which involves cutting, mechanical grinding followed by dimpling and ion beam polishing.

Figure 3. 7 Diced bulk sample plate with a thickness (350 μm)

The preparation of TEM samples starts with cutting or dicing bulk materials into a dimension of around 1 cm by 1 cm with the interface located in the center. Diamond saw is then used to slide it into a plate with the thickness of approximately 350 μm (as shown in Figure 3.6). Subsequently, the plate is mechanically ground down to 100 μm foil using a series of decreased grinding grade sand paper from 180#, 300#, and 800# until 1000#. The foil is then punched into a 3 mm discs with the interface that is still remained across the center (see Figure 3.7). Further mechanical grinding of the foil is carried out using 1000# grade sand paper until it is thinned down to around 35 μm . After all these steps, the thickness is now down to 35 μm .

Figure 3. 8 3mm disc with a thickness of 100 μm

Clean the sample with acetone.

The dimple machine is performed to dimple the interface area on the both sides of the thin foil down 10 μm on each side.

Finally, PIPS (Gatan 691) is used, where two Ar^+ ion beams mill initially the center of the disc with a high energy of 5 KeV and large angles at $\pm 8^\circ$, respectively. When the disc is about to perforate in the center, the beam energy is reduced to 2 KeV at a low angle of $\pm 2^\circ$ until a small hole is visible in the center of the disc. This gentle milling will minimize the damage of the TEM sample. Figure 3.8 show an example how the final TEM sample appears.

Figure 3. 9 TEM sample after ion milling

Chapter 4

Results and Discussion

This chapter consists of two parts, first is the result of discussion of Ni-P/Sn3.5 Ag solder interfacial analysis by SEM and TEM. Second parts is the result and discussion of Ni-W-P/Sn3.5 Ag solder interfacial analysis by SEM and TEM.

In the first part, Crystallization Behavior of Electroless Ni-P will be discussed with the result of Ni-P/Sn3.5 Ag solder interfacial analysis by SEM and TEM, the transition of Ni_3Sn_4 Morphology and Growth Mechanism of Interfacial Compounds will also be discussed.

In the second part, the Crystallization Behavior of Electroless Ni-W-P will be discussed with the result of Ni-P/Sn3.5 Ag solder interfacial analysis by SEM and TEM.

4.1 Ni/P- Sn3.5 Ag solder interfacial analysis by SEM

Figure 4.1. 1 Backscattered electron image (BEI) of the interfacial layer between Sn-3.5Ag solder and Ni-P as reflowed.

Fig. 4.1.1 is a BEI image showing the cross-section of the sample where three zones can be identified in based on contrast differences. Since the higher ordered elements will exhibit to be brighter, we can make sure that the top part is the Sn3.5 Ag solder and the bottom part with darkest color is the Ni-P substrate. Another zone with intermediate color is the transition zone, where the solder and the substrate react with each other at high temperature during the welding process. Based on the reported papers, the estimated compositions are marked at different zones, which is proved by the following experiment

of TEM test. In addition, the precipitation is observed in the Ni-P coating, which is probable Ni_3P particles.

4.1.1. Crystallization Behavior of Electroless Ni-P.

Figure 4.1. 2 SEM BEI of the interfacial layer between Sn-3.5Ag solder and Ni-P after aging at 180 °C for 100 h

Figure 4.1. 3 SEM BEI of the interfacial layer between Sn-3.5Ag solder and Ni-P after aging at 180 °C for 300 h

Figure 4.1. 4 SEM BEI of the interfacial layer between Sn-3.5Ag solder and Ni-P after aging at 180 °C for 1000 h

Figure 4.1.2- Figure 4.1.4 are three BEI images of the interface between solder and substrate after heat treatment at 180°C for 100 hours, 300 hours and 1000 hours, respectively. By comparing the three samples under different conditions, the thickness of the transition zone remains almost the same. However, the surface morphologies for each sample are not identical. It is seen that more particles will precipitate on the surface at higher heat treatment temperature, which is mainly due to the crystallization of the compounds. Therefore, we can conclude that higher temperature contributes to the degree of crystallization.

4.2 Ni/P- Sn3.5 Ag solder interfacial analysis by TEM

Figure 4.2. 1 A bright field TEM image of the cross-section between the Ni/P substrate and the Sn3.5 Ag solder.

In Figure 4.2.1, a bright field TEM, shows the morphology of the interface between Ni/P substrate and the Sn-3.5Ag solder, which is identical to the SEM results consisting of three zones, i.e. solder, transition zone and substrate. These three layers marked by two parallel dash lines are clearly shown two in the Fig. 4.2.1. To verify their respective composition, two square regions 1 and 2 are chosen for EDX analysis.

Figure 4.2. 2 A magnified HR-TEM image of square 1 in Fig. 4.2.1 and two FFT patterns on square A and B, respectively.

As depicted in the high magnification of square 1, the cross-section between the Ni/P substrate and the transition zone can be identified since there is a clear boundary between the two phases. The main contrast between the two areas is the mass thickness. After further identification of these two areas, two different types of phases can be obtained through indexing FFTs. The phase with large d -spacing is matched to monoclinic Ni_3Sn_4 ($a=12.290000\text{\AA}$ $b=4.054000\text{\AA}$ $c=5.170000\text{\AA}$) at the zone axis of $[3\ 1\ 5]$, which is located on the side near Sn-3.5Ag solder. This is probably due to the diffusion of Ni towards the solder matrix and the interaction with Sn at high temperature during the welding process. The other phase near the transition zone is confirmed to be tetragonal Ni_3P ($a=8.955000\text{\AA}$ $b=4.386800\text{\AA}$) in the projection plane of $(2\ 1\ 3)$. The TEM results again reveal that this phenomenon is denoted as “solder reaction-assisted crystallization” of electroless Ni-P, which leads to the transformation of amorphous Ni-P into Ni_3P . This Ni_3P layer was reported to have a well-developed fine columnar structure. Although Ni_3P is widely

reported to be the primary phase formed by solder reaction-assisted crystallization of electroless Ni-P, other Ni-P phases have also been found in the crystallized Ni-P layer. The Ni element from the decomposition of Ni_3P leads to the formation of Ni_3Sn_4 . In the meantime, Ni from the unreacted NiP can diffuse through the Ni_3P layer which also leads to the formation of Ni_3Sn_4 . According to the image, not much clear lattice can be illustrated because of the existence of amorphous-like phase, which are possible the complex phases between Ni and P.

Figure 4.2. 3 A magnified HR-TEM image of square 2 in Fig. 4.2.1 and two FFT patterns on square C and D, respectively.

Another region at substrate- transition zone (i.e. square 2) is imaged at a high resolution in TEM as shown in Fig. 4.2.3. In this image, two kinds of materials are confirmed by the fast fourier transition patterns that are reflected from the two square regions C and D,

respectively. The phase near the Ni substrate is matched to be orthorhombic NiP ($a=6.050000\text{\AA}$ $b=4.881000\text{\AA}$ $c=6.890000\text{\AA}$) in the projection plane of (2 3 1), which is probably produced by the heat treatment at relative low temperature comparing to the transition zone during the welding process. Another phase is tetragonal Ni₃P ($a=8.952\text{\AA}$ $c=4.388\text{\AA}$) that is at zone axis of [2 1 3], the same structure as mentioned at solder-transition zone interface, which is probably generated from the reaction between NiP and Ni at high temperature. Compared to NiP phase, Ni₃P phase is more stable at high temperature. In this case, the depletion of Ni element is consumed by NiP compounds at the interface. The reactions can be described as follows:

Figure 4.2. 4 STEM EDX mapping of the cross-section between NiP substrate and Sn3.5 Ag solder (a) STEM image, (b) Ni, (c) P, (d) Sn.

The STEM-EDX mapping at the Ni-Sn cross-section is illustrated in Fig. 4.2.2. A transition zone with lower contrast of both Ni and Sn can be clearly observed at their interface, indicating the interaction between the Ni substrate and the Sn solder. Meanwhile, the distribution of P (Fig. 4.2.2b) is enriched at the transition zone and deprived from the NiP substrate demonstrating its migration from the substrate towards the transition zone in the welding process, which is consistent with the TEM results above.

4.2.1. Transition of Ni_3Sn_4 Morphology

Several studies (Jang et al., 1999, 2000; He et al., 2004b, d) have examined the morphology of Ni_3Sn_4 IMC in the electroless Ni-P/solder systems. It has been reported that Ni_3Sn_4 grains having needle-type and chunky-type morphologies form at the electroless Ni-P/solder interface after reflow. The formation of needle-type Ni_3Sn_4 grains dominates at the beginning of reflow; however, needle-type Ni_3Sn_4 grains disappear and the number and size of chunky-type Ni_3Sn_4 grains increase with the increase of the reflow duration. In this study, Ni_3Sn_4 IMC with needle-type and chunky-type morphologies are also formed in the as-prepared or reflowed sample and their morphologies are then changed into “scallop-type” after solid-state aging.

Although much has been reported about the morphology of Ni_3Sn_4 IMC in the electroless Ni-P/solder systems, little is known about its transition. In general, other than crystallography, the morphology of IMC formed during soldering reaction mainly depends upon the state of reaction (solid or liquid), solder and UBM compositions, and processing or more accurately the microstructure of reacting materials. Other factors such as reaction temperature and time also influence the IMC morphology. However, their influence is more on grain growth rather than on grain shape. Since Ni_3Sn_4 with needle-type morphology has been reported to form with electroless Ni-P UBM and not with sputtered Ni, it can be easily understood that the needle-type morphology of Ni_3Sn_4 is related to the microstructure of electroless Ni-P. The electroless Ni-P UBM (12.5 at.% < P < 19 at.%) used in the electronic industry normally has amorphous structure, which transforms into crystalline Ni_3P and Ni-Sn-P layers due to the soldering reaction. The crystallized electroless Ni-P layer has fine columnar grains of nm size. Thus, considering the microstructure of Ni_3P layer, the formation of needle-type Ni_3Sn_4 IMC in the electroless Ni-P/solder system can be understood. At the beginning of soldering reaction when the Ni_3P grain is of a few tens of nm and the thickness of Ni-P layer is negligible, it is reasonable that a large number of needle-type Ni_3Sn_4 IMC are formed due to the

presence of a large number of grain boundaries in Ni_3P layer. These grain boundaries are perpendicular to the reaction interface and Ni atoms diffuse out from electroless Ni-P layer through them. Therefore, at the beginning of soldering reaction, Ni atoms are trapped by Sn atoms at the exit of Ni_3P grain boundaries and unidirectional flow of Ni from Ni_3P grain boundaries results in the needle-type morphology of Ni_3Sn_4 . After the formation of needle-type Ni_3Sn_4 , as soldering reaction precedes, needle-type Ni_3Sn_4 grains disappear and chunky-type Ni_3Sn_4 grains grow due to the well-known grain-coarsening phenomenon.

In the case of solid-state aging, the needle-type and/or chunky-type morphology of Ni_3Sn_4 change into scallop-type due to the change in interfacial energy between Sn-3.5Ag solder and Ni_3Sn_4 intermetallic. The interfacial energy of intermetallics is highly anisotropic with molten pure Sn and it decreases with increasing the concentration of alloying element. Thus, the interfacial energy between Ni_3Sn_4 and molten Sn-Ag solder with a small amount of Ag (less than 3.5wt.%) can be understood to be highly anisotropic and this causes the Ni_3Sn_4 morphology to be faceted chunky-type. However, during solid-state aging, the interfacial energy between Ni_3Sn_4 and solid Sn-Ag solder becomes isotropic and consequently Ni_3Sn_4 morphology changes from faceted chunky-type to curved scallop-type.

4.2.2 Growth Mechanism of Interfacial Compounds

From the experiment, two compounds (Ni_3Sn_4 and Ni_3P) are found during the interfacial reaction. It is known that during electroless Ni-P/Sn-3.5Ag solder interfacial reactions, Sn reacts with Ni of electroless Ni-P forming Ni_3Sn_4 IMC. The transformation of Ni atoms into higher P containing Ni-P (Ni_3P) layer is due to its depletion from electroless Ni-P layer.

From the investigation, the formation of Ni_3Sn_4 not only comes from the interfacial reaction between Ni of electroless Ni-P and Sn of solder. Meanwhile, Sn also react with Ni_3P and which will form Ni_3Sn_4 as well. As soon as the transformation from the electroless Ni-P layer to Ni_3P is completed, the formation of Ni_3Sn_4 could not be accomplish by the Ni atoms from electroless Ni-P. Therefore, the formation of Ni_3Sn_4 comes from the reaction between Sn and Ni_3P layer. That is, the fast growth of the Ni_3Sn_4 layer is depend on the expense of the Ni_3P layer.

4.3 Ni/W/P- Sn3.5 Ag solder interfacial analysis

4.3.1 Result and discussion of Ni-W-P

Figure 4.3. 1 EDX result of Ni-W-P layer.

To identify the compositional element of Ni-W-P. EDX has been used, and the following results are obtained: Ni has a weight percentage of 59.43%, P has a weight percentage of 12.52% and W has a weight percentage of 28.05%.

Figure 4.3. 2 Backscattered electron image (BEI) of the interfacial layer between Sn-3.5Ag solder and Ni-W-P as reflowed.

From Figure 4.3.2, the thickness of Ni-W-P is about 14μm as reflowed. The electroless Ni-W-P thin film has a very uniform thickness. There is a very obvious line to show the interface between Ni-W-P and Sn-3.5Ag.

Figure 4.3. 3 Backscattered electron image (BEI) of the interfacial layer between Sn-3.5Ag solder and Ni-P at 180 °C for 1000 h

From the above images, the thickness of Ni-W-P is about 14μm as reflowed. After it has been aged at 180 °C for up to 1000 h. The thickness of NiP decreases to 12.1 μm. Ni-W-P is consumed. And inter metallic compounds are formed during aging process. To find the exact IMCs. TEM technique has to be done.

Figure 4.3. 4 A bright field TEM image of the cross-section between the Ni/W/P substrate and the Sn3.5 Ag solder.

As shown in the low magnification TEM image above, three zones- Ni/W/P substrate, middle transition zone and the solder zone can all be observed from the top right to the bottom left. To be more detailed, the width of transition zone can be measured to be around ~200 nm with the lowest contrast and the most complicated morphologies due to the heat treatment reactions at this zone under high temperature. In order to investigate the composition and structure of the above zones, three square regions- substrate-

transition zone interface (square 1), transition zone (square 2) and transition zone-solder interface (square 3) are chosen to study their microstructures, respectively.

Figure 4.3. 5 A magnified HR-TEM image of square 1 in Fig. 4.3.1 and three FFT patterns on square 1, 2 and 3, respectively.

As depicted in the high magnification above, the cross-section between the Ni/W/P substrate and the transition zone can be identified, although there is no clearly boundary to be observed due to the migration and reactions among the different compositions and structures. According to the image, low sharp contrast can be seen because of the existence of amorphous-like phase. However, three types of structures can be found and identified at this region. Firstly, hexagonal NiWP_8 ($a=6.221 \text{ \AA}$ $c=8.749 \text{ \AA}$) is seek out to be at the innermost location (square 1), which is likely the composition of the Ni/W/P substrate, at zone axis of $[3 -2 1]$. In addition, two more compositions are also be found at

the place near the transition zone, which are orthorhombic NiP ($a=6.05 \text{ \AA}$ $b=4.881 \text{ \AA}$ $c=6.89 \text{ \AA}$) and orthorhombic WP ($a=5.731 \text{ \AA}$ $b=3.248 \text{ \AA}$ $c=6.227 \text{ \AA}$) in the projection planes of (1 1 2) and (1 3 1), respectively. Identical to the discovery for NiP/Sn-3.5 Ag transition zone, NiP also exists at the transition zone for this substrate. Similarly, WP is also found to exist at this zone together with NiP. The reason of the existence of the above two composition is possibly resulted from the deposition of NiWP_8 .

Figure 4.3. 6 A magnified HR-TEM image of square 2 in Fig. 4.3.1 and three FFT patterns on square 1 and 2, respectively.

Another region in the middle transition zone is chosen and analyzed by high magnification TEM image. At this transition zone, two kind of materials are found and confirmed by the fast fourier transition patterns that reflected from the two square region 1 and 2, respectively. The first one is tetragonal Ni_3P ($a=8.952 \text{ \AA}$ $c=4.388 \text{ \AA}$) that is at

zone axis of $[3\ -2\ 1]$, which is probably generated from the reaction between NiP and Ni at high temperature as mentioned above. What's more, another binary compound monoclinic NiW_2P_3 ($a=12.598\ \text{\AA}$ $b=3.24\ \text{\AA}$ $c=8.526\ \text{\AA}$) is identified to exist in the projection plane of $(2\ -1\ -1\ 0)$. It is interesting to find that no Ni_3P is discovered at this transition zone, which is different from the results for the Ni/P substrate case. The reason for this phenomenon may be due to the competition of combining with P of the other component- W, which can be demonstrated by the existence of WP at transition zone in Fig. 4.3.2. Furthermore, no Sn related species is found to exist at the middle transition zone indicates that the migration of P towards the transition zone is faster and further than that of Sn.

Figure 4.3. 7 A magnified HR-TEM image of square 3 in Fig. 4.3.1 and three FFT patterns on square 1 and 2, respectively.

The last region to be analyzed is the interface between the transition zone and the Sn3.5 Ag solder zone. By using FFT patterns that converted from the HR-TEM image, two types of components can be confirmed to be presented. One is the monoclinic Ni_3Sn_4 ($a=12.2 \text{ \AA}$ $b=4.056 \text{ \AA}$ $c=5.212 \text{ \AA}$) at the zone axis of $[0\ 0\ 0\ 1]$, which turns out to be the same as the product in the transition zone of Ni/P- Sn 3.5 Ag system. This product may be resulted from the reaction between Sn in the solder and the Ni that diffuses from the NiP substrate. At this point, we can conclude that the migration or diffusion capacity of Ni is higher than that of Sn in the current system. The other kind of product is rhombohedral Sn_4P_3 ($a=3.9677 \text{ \AA}$ $c=35.331 \text{ \AA}$) in the projection plane of $(3\ 1\ 2)$, which is a new species that is not observed in the Ni/P- Sn 3.5 Ag system. Similar to the diffusion of Ni atoms, the element P is also come from the diffusion of Ni/P substrate towards the Sn3.5 Ag solder. However, the reason why Sn_4P_3 can only appear in the Ni/W/P- Sn3.5 Ag system is not available in the current experiment, which still requires the further study with other techniques.

The NiW_2P_3 growth activation energy in the reaction of solid state solder is calculated to be 58.2 kJ/mol, along with a prefactor of $2.46 \times 10^{-15} \text{ cm}^2/\text{s}$. Notice that the prefactors for growths of both the Ni_3Sn_4 and NiW_2P_3 layers are much lower than the prefactor of Ni_3Sn_4 formation in soldering with Ni-P, it is because of the decreasing availability of Ni atoms at the soldering interface as a result of the presence of W during metallization process.

Figure 4.3. 8 STEM EDX mapping of the cross-section between NiP substrate and Sn3.5 Ag solder (a) STEM image, (b) Ni, (c) P, (d) Sn.

Like the previous analysis, dark field STEM EDX is also occupied to investigate the element distribution within the interface between the substrate and the solder. As illustrated in Fig. 4.3.5a, the brighter region means the distribution of higher order elements, indicating the enrichment of W at this region, which can be proved by the distribution of element W at Fig. 4.3.5b. Additionally, the distribution of Ni is identical to that of W in the transition zone. In comparison with the high contrast of Ni and W, weaker signals of Sn and P can be observed in Fig. 4.3.5c and d, respectively, which means the contents of this two elements are much lower than those of Ni and W. To be noticed, the elemental distribution can also prove the point of view that the diffusion of Ni, W and P is dominant during the welding process.

Overall, for Ni-W-P/Sn-3.5Ag interface. The Ni_3P and Ni_3Sn_4 IMCs are much less than that in Ni-P. The IMCs of Sn_4P_3 , WP, NiWP_8 , NiW_2P_3 have a much higher mechanical strength. It may form a barrier for Ni diffuse into Sn-3.5Ag to from the weaker Ni_3P and Ni_3Sn_4 .

4.4 Result and discussion of Ni-P and Ni-W-P

For Ni-P/Sn3.5Ag interfacial reaction

1. Two main IMCs formed in the interface of Ni-P/Sn-3.5Ag are Ni_3Sn_4 and Ni_3P . The formation of Ni_3Sn_4 is due to the reaction between Ni and Sn. While the formation of Ni_3P is due to the formation of Sn and Ni which is the depletion from electroless Ni-P.
2. Ni_3Sn_4 grains with needle-type and chunky-type morphologies form during reflow; however, their morphologies change into scallop-type after solid-state aging.
3. The activation energies of Ni_3Sn_4 and Ni_3P compounds are calculated to be 98.9 and 94.3 kJ/mol, respectively.
4. Interfacial reactions degrade the mechanical properties of Cu/electroless Ni-P/Sn-3.5Ag solder joint due to the extensive growth of Ni_3Sn_4 and Ni_3P . These two IMCs have very low mechanical strength. When these two IMCs stuck at interface, they will lead to brittle fracture in the end.
5. The growth of Ni_3Sn_4 IMC results in a mixed fracture at the $\text{Ni}_3\text{Sn}_4/\text{Sn-3.5Ag}$ interface. The depletion of Cu from the Cu surface form a layer of Kirkendall voids at the Cu/ Ni_3P interface, which degrades the joint strength further. Also, a brittle fracture is caused at the Cu/ Ni_3P interface.

For Ni-W-P/Sn3.5Ag interfacial reaction

1. There are several interfacial compounds, Sn_4P_3 , WP, NiWP_8 , NiW_2P_3 , Ni_3P and Ni_3Sn_4 are formed during Ni-W-P/Sn-3.5Ag interfacial reaction. For Ni atoms diffuse out from the Ni-W-P layer towards solder and react with the Sn atoms from the solder to form Ni_3Sn_4 . Meanwhile, the formation of Ni_3Sn_4 causes the depletion of Ni from the surface of the Ni-W-P layer, leading to continued growth of the ternary $(\text{Ni,W})_3\text{P}$ layer. This reaction mechanism has been supported by the mass balance of Ni during Ni-W-P/Sn-3.5Ag interfacial reaction.

2. After prolonged aging, unlike at the Ni-P/Sn-3.5Ag interface, no voids were found at the Ni-W-P/Sn-3.5Ag interface. The Ni_3Sn_4 compound grows much more slowly. In addition, the consumption of the Ni-W-P layer was found to be much slower than that of the Ni-P layer. These facts indicate a significantly slow out-diffusion of Ni atoms at the Ni-W-P/Sn-3.5Ag interface; hence, Ni-W-P layer stands out as an impressive diffusion barrier for lead-free soldering.
3. Both growths of the Ni_3Sn_4 and NiW_2P_3 layers at the Ni-W-P/Sn-3.5Ag interface are diffusion-controlled. The activation energies for the growths of Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers during solid-state reaction are calculated to be 62.3 kJ/mol and 58.2 kJ/mol, respectively.

Chapter 5

Conclusions

From all the SEM and TEM images, with the help of fundamental analysis and calculations, Ni-W-P has a great improvement than in Ni-P with Sn3.5Ag solder joint.

Which has been reported that, for Ni-P the main problem of the failure in the interface is due to the IMCs of Ni_3P and Ni_3Sn_4 , while in Ni-W-P, Ni_3P and Ni_3Sn_4 are found much less,

The IMCs formed in Ni-W-P (Sn_4P_3 , WP, NiWP8, NiW2P3) are calculated with are much high mechanical strength than Ni_3P and Ni_3Sn_4 . Whats more, these IMCs could form a barrier for the Ni to diffuse into Sn-3.5Ag to from the weaker IMCs.

In the present work, scanning electron microscopy and transmission electron microscopy were mainly employed to study the three IMC layers at the welding joints. With the help of SEM technique at BEI mode, Sn-3.5Ag solder, transition zone and Ni/P substrate can be clearly distinguished by contrast. Also, the existence of voids at the transition zone is inevitable during the heat treatment process. What's more, we find that the high temperature contributes to the crystallization of the interface.

Phase and composition information is revealed by TEM. For Ni/P-Sn3.5 Ag, the main product at transition zone is Ni_3P , which is produced from NiP. For the zone near solder area, Ni_3Sn_4 is the main component while NiP is dominant near the substrate side. In contrast, the results in Ni/W/P- Sn3.5Ag system is much more complicated in phase and composition. To be identical to the Ni/P-Sn3.5Ag case, Ni_3P is also the main product in transition zone but it is not the unique product. NiW_2P_3 is also discovery at this zone due to the contribution of element W. In addition, WP and NiWP_8 are both found to be located near the substrate. Furthermore, a novel species Sn_4P_3 is confirmed at the zone near solder matrix, which is not found in Ni/P- Sn 3.5 Ag system, probably ascribed to the contribution of element W. In conclusion, more phases in Ni/W/P- Sn 3.5 Ag system are found, which is the possible reason for the better performance. Again, the Ni_3P and Ni_3Sn_4 IMCs are much less than that in Ni-P. The IMCs of Sn_4P_3 , WP, NiWP_8 , NiW_2P_3 have a much higher mechanical strength. It may form a barrier for Ni diffuse into Sn-3.5Ag to from the weaker Ni_3P and Ni_3Sn_4 .

Chapter 6

Future Work

The main objective of this project is to study the formation of intermetallic compounds, mechanisms of interfacial reaction and reliability of solder joints formed by lead-free solders with Ni-based UBMs, especially electroless Ni-P UBM. Based on these aims as well as problems and limitation encountered in the work that has been done, following work might be recommended for further studies: Systematic work on reaction of lead-free solders with different P content Ni-P alloys should be performed. Current study finds the Ni_3P play an important role in interfacial reaction. Different initial P in the UBM would change the reaction kinetics, which in turn affect the joint strength. Ternary Ni-P such as Ni-Co-P is reported to have better mechanical properties and such sample of preparation has been done. TEM and SEM works have to be done to compare its performance with Ni-P.

This work limits the investigation of joint strength to monotonic tensile test. However, in industrial reliability test and/or under usage condition, cycling stress is experienced by the solder joint. Therefore, fatigue study of solder bumps with Ni-based UBM worth studying in the future.

References

1. Y. Yang, J .N. Balaraju, S. C. Chong, H. Xu, C. Q. Liu, Vadim, V. Silberschmidt and Z. Chen(2013). "Significantly retarded interfacial reaction between an electroless Ni-W-P metallization and lead-free Sn-3.5Ag solder", Journal of Alloys and Compounds, 50(3), 1201-1210.
2. A. Kumar(2007). "Interdependent Intermetallic Compound Growth in an Electroless Ni-P/Sn-3.5Ag Reaction Couple", Journal of ElectronicMaterials, 27(4), 648-658.
- 3 . A. Kumar(2004). " IEEE Transactions on Components and Packaging Technologies", 88(2), 1777-1782.
- 4 . Z. Chen(2005). "Effect of Ni-P Thickness on the Tensile Strength of Cu/Electroless Ni-P/Sn- 3.5Ag Solder Joint", 2005 7th Electronic Packaging Technology Conference, 31(9), 789-798.
- 5 . C. E. Ho(2006). "Interfacial reaction issues f or lead-free electronic solders", Journal of Materials Science Materials in Electronics, 14(3-4), 488-498.
6. A. Kumar,(2004). "Effect of electromigration on interfacial reactions between electroless Ni-P and Sn-3.5% Ag solder", Thin Solid Films, 21(2), 1298-1305.
7. A. Kumar,(2008). "Influence of solid-state interf acial reactions on the tensile strength of Cu/electroless Ni-P/Sn-3.5Ag solder joint", Materials Science & Engineering ,77(8-9), 3498-3509.
8. Y. Yang(2011). "Electroless Ni-W-P alloy as a more enduring and reliable soldering metallization", 2011 IEEE 13th Electronics Packaging Technology Conference, 12(1-2), 122-130.
9. Y. Yang(2009). "Interface reaction of Pb-free Sn-3.5Ag solder with Ni-Sn-P metallization", 2009 11th Electronics Packaging Technology Conference, 8(0), 198-205
10. Y. Yang, J. N. Balaraju, Y.Z. Huang, Y. Y. Tay, Y.Q. Shen, Z. Tsakadze, and Z. Chen(2014). "Interface Reaction Between Electroless Ni-Sn-P Metallization and Lead-Free Sn-3.5Ag Solder with Suppressed Ni₃P Formation", Journal of Electronic

Materials, 48(8), 177-185.

11. Kumar, A(2006). "Effect of Ni-P thickness on solid- state interfacial reactions between Sn-3.5Ag solder and electroless Ni-P metallization on Cu substrate", Thin Solid Films, 28(3), 1398-1405.

12. Z. Chen(2007). "Interf ace Reactions and Shear Strength of Lead-Free Sn-3.5Ag Solder with Ni-W-P Metallization", 2007 9th Electronics Packaging Technology Conference, 125(2), 115-119.

13. A. Kumar(2005). "Barrier properties of thin Au/Ni-P under bump metallization for Sn-3.5Ag solder", Surface & Coatings Technology, 88(8), 3408-3411.

15. M. Wu(2006). "Interfacial reactions between Sn- 2.5Ag-2.0Ni solder and electroless Ni(P) deposited on SiC/p/Al composites", Transactions of Nonferrous Metals Society of China, 71(4), 199-200.

16. P. Sun(2006). "High temperature aging study of intermetallic compound formation of Sn-3.5Ag and Sn-4.0Ag-0.5Cu solders on electroless Ni(P) metallization", Journal of Alloys and Compounds, 64(0), 117-120.

17. M. Alam(2008). "Effect of 0.5 wt% Cu in Sn-3.5%Ag Solder to Retard Interfacial Reactions With the Electroless Ni-P Metallization f or BGA Solder Joints Application", IEEE Transactions on Components and Packaging Technologies, 32(3), 3444-3450.

18. J. Bae(2012). "The role of a ternary Ni-Sn-P layer as a dif f usion barrier in the Sn-Ag solder/electroless Ni-P system : A ternary Ni- Sn-P layer as a dif f usion barrier in the Sn-Ag solder", Surface and Interface Analysis, 109(2), 408-411

19. L. Tomi and V. Vuorinen(2001). "Combined Thermodynamic-Kinetic Analysis of the Interfacial Reactions between Ni Metallization and Various Lead-Free Solders", 8(1), 188-205

20. J. W. Jang(1999). "Solder reaction-assisted crystallization of electroless Ni-P under bump metallization in low cost flip chip technology", Journal of Applied Physics, 14(3-4), 488-498

21. H. Y. Chen and C. Chen(2012). "Kinetic study of the intermetallic compound formation between eutectic Sn-3.5Ag alloys and electroplated Ni metallization in flip-chip solder joints", *Journal of Materials Research*,239(1), 93-98.
22. C.B. Lee, In-Young Lee, S.B. Jung, and C.C. Shur(2002). "Effect of Surface Finishes on Ball Shear Strength in BGA Joints with Sn-3.5Ag Solder.", *Materials transactions*, 258(20), 7962-7967.
23. Z. Chen(2004). "Morphology and kinetic study of the interfacial reaction between the Sn-3.5Ag solder and electroless Ni-P metallization", *journal of Electronic Materials*, 39(5), 385.
24. K. C. Hung, Y. C. Chan, C. W. Tang, and H. C. Ong(2000). "Correlation between Ni₃Sn₄ intermetallics and Ni₃P due to solder reaction-assisted crystallization of electroless Ni metallization in advanced packages", *Journal of Materials Research*,19(19), 1755-1757.
25. Z. Chen(2006). "Effect of phosphorus content on Cu/Ni-P/Sn-3.5Ag solder joint strength after multiple reflows", *Journal of Electronic Materials*, 12/2006
26. V. Kripesh. "Evolution of Microstructure and Mechanical Properties of Eutectic Sn-Pb Solder Joint Aged under Thermal Gradient", 2007 9th Electronics Packaging Technology Conference, 15(11), 2534-2539
27. X. Hu, and Y.C. Chan(2014). "Reinforced solder joint performance by incorporation of ZrO₂ nanoparticles in electroless Ni-P composite layer", *Journal of Materials Research*, 88(11), 6359-6363.
28. N. Hiroshi(2007) . "Morphology and Pull Strength of Sn-Ag(-Co) Solder Joint with Copper Pad", *Journal of Electronic Materials*, 22(4), 568-574.
29. C.H.Wang, S.E. Huang, and C.H Chiu(2015). "Influence of the P content on phase formation in the interfacial reactions between Sn and electroless Co(P) metallization on Cu substrate", *Journal of Alloys and Compounds*, 29(1), 2569-2574.
30. V. Kripesh(2010). "Effect of electric current on the mechanical properties and

- interfacial microstructure of Ni-P/Sn-3.5Ag and Ni/Sn-3.5Ag solder joints", 2006 8th Electronics Packaging Technology Conference, 31(11), 2867-2875.
31. J. K. Kivilahti(2001). "Intermetallic reactions between lead-free SnAgCu solder and Ni(P)/Au surface finish on PWBs", 2001 Proceedings 51st Electronic Components and Technology Conference, 18(11), 2540-2543.
32. Y.C. Hu, C.T. Lu, T.S. Huang, C.Y. Chen, W.N. Chuang, C.Y. Hsiao, C.P. Lin, and C.Y. Liu(2014). "Interfacial Reactions Between Columnar or Layered Ni(P) Layers and Sn-Ag- Cu Solder", Journal of Electronic Materials, 258(10), 962-967
33. H. Steen(2005). "Interactions between liquid Sn-Bi based solders and contact metals for high temperature applications", Proceedings Electronic Components and Technology, 283(1-2), 140-144.
34. J. M. Koo(2005). "Effect of substrate metallization on mechanical properties of Sn-3.5Ag BGA solder joints with multiple reflows", Microelectronic Engineering, 18(1), 4-7.
35. Y. F. Shen(2010). "Nanoscratching deformation and fracture toughness of electroless Ni-P coatings", Surface & Coatings Technology, 177-178(0), 532-536.
36. W. Xu, Q. F. Zhong, T. An, and C.Y. Liu(2011). "Morphology and nanoindentation properties of intermetallic compounds in solder joints", 2011 12th International Conference on Electronic Packaging Technology and High Density Packaging, 239(2), 94-98
37. P. P. Conway(2005). "Interfacial reactions between Pb free solders and metallized substrate surfaces", 2005 6th International Conference on Electronic Packaging Technology, 39(5), 385.
38. J. G. Duh(1993). "Structure, hardness and adhesion in electroless nickel interlayer modified TiN coating on mild steel", Surface & Coatings Technology, 25(5), 2573-2584.
39. B. L. Young(2001). "Interfacial reaction and microstructural evolution for electroplated Ni and electroless Ni in the under bump metallurgy with 42Sn58Bi solder during annealing", Journal of Electronic Materials, 148(2-3), 143-148.

-
40. Y. Yang, J. N. Balaraju, and Z. Chen(2010). "Reflow study of Pb-free Sn-3.5Ag solder with Ni-Sn-P metallization", 2010 12th Electronics Packaging Technology Conference,20(1-2), 569-574.
 41. Y. C. Sohn, J. Yu, S. K. Kang, W. K. Choi and D. Y. Shih(2003). "Study of the reaction mechanism between electroless NiP and Sn and its effect on the crystallization of NiP", Journal of Materials Research, 51(12), 6366-6376.
 42. Y. C. Lin(2007). "Morphological and Microstructural Evolution of Phosphorous-Rich Layer in SnAgCu/Ni-P UBM Solder Joint", Journal of Electronic Materials, 36(11), 1469-1475.
 43. Y. L. Oh(2009). "Inhomogeneous Consumption of the Electroless Ni-P Layer at the Solder Joint Formed with Sn-3.5Ag-0.7Cu", Journal of Electronic Materials, 08/11/2009
 44. K. M. Klimov(2006). "Effect of a high-density electric current on the plastic deformation of aluminum", Strength of Materials, 33(12), 1465-1472.
 45. Zhang, L(2012). "Development of Sn Ag-based lead free solders in electronics packaging", Microelectronics Reliability,11(8), 587-593.
 46. J.M. Song, Y. R. Liu, C.W. Su, Y. S. Lai, and Ying-Ta Chiu(2008). "Intermetallic formation induced substrate dissolution in electroless Ni(P)-solder interconnections", Journal of Materials Research, 30(9), 1129-1132.
 47. J. F. Li, S.H. Mannan, M.P. Clode, C. Liu, K. D. C. Chen ,D. A. Whalley, D.A. Hutt, and P.P.Conway(2008). "Interfacial Reaction Between Molten Sn-Bi Based Solders and Electroless Ni-P Coatings or Liquid Solder Interconnects", IEEE Transactions on Components and Packaging Technologies, 20(8), 1931-1934.
 48. F. Lang(2011). "Improvement in Joint Reliability of SiC Power Devices by a Diffusion Barrier Between Au-Ge Solder and Cu/Ni(P)- Metalized Ceramic Substrates", Journal of Electronic Materials, 396(1-2), 122-127.