Study of process responses, intermetallic formation and reliability of palladium-coated copper wire bonds

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NANYANG
TECHNOLOGICAL
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**STUDY OF PROCESS RESPONSES, INTERMETALLIC
FORMATION AND RELIABILITY OF PALLADIUM-COATED
COPPER WIRE BONDS**

LIM BEE YEN ADELINE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

This thesis aims to address the knowledge gaps in terms of bondability, intermetallic formation and corrosion performance between palladium-coated Cu (Pd-Cu) and bare Cu wire bonds. The research specifically targets industrial fine pitch interconnect applications where a bonding wire (bare Cu and Pd-Cu) of approximately 15 μm diameter is used.

In this research project, the effect of key process parameters such as Electronic Flame Off (EFO) current and cover gas type on the palladium distribution in Pd-Cu Free Air Ball (FAB) and bonded balls was studied. It was observed that Electronic Flame Off (EFO) current has a significant effect on the palladium distribution in Pd-Cu FABs. In addition, the hardness of Pd-Cu FABs is strongly affected by the EFO current and palladium distribution.

Cu-Al intermetallic compounds (IMCs), typically CuAl_2 , CuAl and Cu_9Al_4 can be present between copper bonded ball and aluminum metallization in the as-bonded state and after thermal annealing. Bulk alloys of Cu and Cu-Al IMCs with varying concentrations of palladium (0, 1, 3 and 10 wt.% replacement of Cu) were prepared. The mechanical properties of these Cu and Cu-Al IMCs were studied using nano-indentation. Effects of the addition of palladium on these mechanical properties were also investigated. Among the three Cu-Al IMCs studied, CuAl (H~8.5 GPa) was found to be much harder than CuAl_2 and Cu_9Al_4 (H~6.0 GPa). Young's moduli of CuAl and Cu_9Al_4 IMCs were around 155 GPa and are much stiffer than the one for CuAl_2 (~110 GPa). The addition of a few percent of Pd only slightly increases the hardness and Young's modulus of the IMCs.

The humidity reliability of bulk Cu, Al and the Cu-Al IMCs with various concentrations of Pd addition was investigated using a conventional three-electrode cell and an acidic chloride solution as the electrolyte. Among the three Cu-Al IMCs, Cu_9Al_4 has the highest corrosion rate followed by CuAl_2 and CuAl. Pure Al is also more easily

corroded than pure Cu. Palladium was shown to slightly improve the corrosion resistance of the metals and the Cu-Al IMCs.

Interfacial evolution and bond reliability in Pd-Cu wire bonds during isothermal annealing at 175°C was investigated and compared to that of bare Cu wire bonds. The IMC thickness for Pd-Cu bonds with Pd at the bond interface was found to be thinner as compared to that for Pd-Cu wire bonds with no Pd at the bond interface. The presence of palladium at the bond interface has slowed down the IMC growth. Corresponding bond pull test finds that Pd-Cu wire bonds with Pd at the bond interface have best preserved the bond strength after long hours of annealing due to the beneficial presence of Pd.

This research project provides fundamental information on the bondability, intermetallic growth and corrosion susceptibility of Pd-Cu wire bonds which will be useful to ensure good quality Pd-Cu wire bonding and reliability. Pd addition was shown to improve the corrosion resistance and thermal reliability of copper wire bonds, and its distribution can be controlled through the bonding process. Based on the generated understandings, guidelines for packaging engineers for reliable bonding using Pd-coated Cu bonding wires were generated.

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Abbreviations

atm. %	Atomic Percent
BSR	Ball Size Ratio
CSM	Constant Stiffness Measurement
CV	Constant Velocity
EBSD	Electron Backscattered Diffraction
EDX	Energy Dispersive X-ray Spectroscopy
EFO	Electronic Flame Off
EIS	Electrical Impedance Spectroscopy
E _{oc}	Open circuit potential
EPMA	Electron Probe Microanalysis
FAB	Free Air Ball
FCC	Face-Centered Cubic
FIB	Focused Ion Beam
HAADF	High Angle Annular Dark Field
HAST	Highly Accelerated Stress Test
HRTEM	High Resolution Transmission Electron Microscopy
HTS	High Temperature Storage
RH	Relative Humidity
IMC	Intermetallic Compound
NSOP	Non-stick on Pad
PCT	Pressure Cooker Test
SEM	Scanning Electron Microscopy
SPA	Shear per Area
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
USG	Ultrasonic Energy
XRD	X-ray Diffraction
wt.%	Weight Percent

Chapter 1

Introduction

Wire bonding is the technology of making electrical interconnections between the integrated circuits (ICs) and external circuits in the substrate. Thermosonic ball bonding was developed by Coucoulas in 1970 [1] and is now being employed in 90% of the wire bonded devices. This bonding method uses a combination of ultrasonic, bonding force and thermal energy.

Gold wire has traditionally been the bonding material of choice used in wire bonding. However, due to the continuous increase in gold prices, copper wire has been rapidly adopted in fine-pitch applications and volume production [2]. In recent years, palladium-coated copper (Pd-Cu) wire is widely used in fine-pitch applications to overcome some constraints posed by bare Cu wire. Pd-Cu wire has a longer shelf life compared to bare Cu wire due to the noble metal coating and is perceived to perform better in humidity reliability test compared to bare Cu wire [3-8].

The presence of a Pd rich layer at the bond interface in Pd-Cu wire bonds can affect the intermetallic compounds formed in the as-bonded state, the hardness, bondability and reliability of the wire bonds. This thesis addresses the existing knowledge gap in terms of the bondability, interfacial evolution and reliability of thermosonic Pd-Cu ball bonding on Al metallization. In addition, the effect of key process parameters on palladium distribution in Pd-Cu Free Air Balls will be studied. The answers to these questions are fundamental in material science, and also bear significant implication to the long reliability of electronic packages and devices.

1.1 Problem Statement

Thermosonic ball bonding is a key technology for fabricating electrical interconnects between integrated circuit chips and substrates in microelectronics packages. Electrical connectivity is obtained by melting of the wire tip to form a Free Air Ball (FAB) using an electronic spark, and then thermosonically welding the FAB onto a metallization pad on the chip using a combination of impact force, ultrasonic energy and heat. This is followed by wire looping and stitch bonding onto substrate pad or lead finger. Figure 1.1 shows a schematic illustration of the thermosonic ball bonding process.

Figure 1.1 Schematic illustration of the thermosonic wire bonding process [1]

Gold wire has been a popular choice of bonding wire for many years and knowledge about gold wire bonding process is extensive and mature. Equipment and process were developed and optimized for the gold wire bonding process. In the past few

years, bare Cu wire is widely used in fine pitch applications due to its lower cost compared to gold. In addition, it has better electrical and thermal conductivity compared to gold wire [2]. However, copper wire has a high propensity to oxidize and studies have shown that it is susceptible to corrosion under molded humidity and electrically biased conditions and package reliability is a concern. Chloride from the epoxy mold compounds are known to attack the Cu rich IMC at the first bond [3-8]. In recent years, Pd-Cu wire has seen entry into the market and is widely adopted for fine pitch copper applications. It has a longer shelf life compared to bare copper wire due to the noble metal coating and is believed to have enhanced bond reliability under humid and electrically biased conditions [3-8].

It has been reported in literature that electronic flame off (EFO) current and cover gas type can affect palladium diffusion in Pd-Cu FAB, with EFO current being the major contributing factor. However, the effect of process parameters on palladium diffusion in Pd-Cu wire during FAB formation has been ambiguous and there is a lack of proper mechanism to describe the diffusion of palladium in the bulk copper at different processing parameters. Localized diffusion of Pd in Pd-Cu FAB can affect the overall FAB hardness before impacting on the Al bond pad. This could have an effect on Al bond pad damage and degradation. However there is no reported literature on the overall Pd-Cu FAB hardness with varying process parameters. While the IMC growth in bare Cu wire bonds on aluminum is well established, there is little literature in terms of the morphology and growth of intermetallic phase between Pd-Cu wire and aluminum pad. Palladium addition can affect the formation and growth of Cu-Al IMCs which subsequently affects the bond integrity and stress built up in the underlying bond pad layers during thermal annealing. Such mechanical data in terms of hardness and stiffness of individual Cu-Al IMCs with presence of Pd has not been reported before in papers. Industrial reliability tests of Cu wire in molded compounds have been documented. Cu wire was known to be susceptible to corrosion under humidity and electrically biased conditions. However, reliability of Pd-Cu wire bonds in industrial humid reliability test has been ambiguous. The reliability results based on different literature are not conclusive and there is still insufficient data to draw clear and reliable conclusions on the effect of Pd and Pd distribution on Pd-Cu wire bond reliability.

This project aims to bridge the knowledge gaps between Cu and Pd-Cu wire bonding and to understand the impact of palladium to copper wire bondability, intermetallic formations and long term reliability. With this understanding, operating guidelines can be defined to ensure long-term reliability of Pd-Cu wire bonded devices.

1.2 Objectives and Scope

This project addresses the knowledge gap regarding mechanical properties, bondability, interfacial evolution and reliability in thermosonic Pd-Cu ball bonding on aluminum bond pads. Cu and Pd-Cu wires of 15 μm in diameter are used in this research project as it is being qualified and used in fine-pitch applications. Based on the above details, the main objectives of this project are formulated:

1. To study the effect of key process parameters (e.g. EFO current and cover gas types) on palladium distribution, grain size and grain orientation in Pd-Cu FAB.
2. To understand the influence of palladium distribution and grain structure on Pd-Cu FAB hardness and wire bondability.
3. To compare the mechanical properties of Cu and Cu-Al intermetallic compounds and understand the effect of Pd addition on these properties.
4. To study the corrosion performance of Cu, Al and Cu-Al intermetallic compounds with varying concentrations of Pd in an acidic chloride medium, mimicking conditions in molded humidity reliability tests.
5. To investigate the effect of palladium distribution on Cu-Al intermetallic compound (IMC) formation and growth with thermal annealing.
6. To generate guidelines for reliable bonding using Pd-coated Cu wires based on the generated understandings as stated above.

Figure 1.2 shows a flow chart of the project objectives and scope.

Figure 1.2 Outline of the project objectives and scope.

1.3 Dissertation Overview

The thesis contains six sections as shown in Figure 1.3.

Chapter 1 provides motivation and objectives for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning copper wire bonding, provides an overview of the interfacial evolution and industrial reliability tests of copper wire bonds. The review of interfacial reactions includes the formation and growth kinetics of Cu-Al intermetallics. Some studies done on Pd-Cu wire bonding will also be reviewed.

Chapter 3 gives a detailed description of the materials and equipment setup, sample preparation techniques, material characterization and analysis techniques.

Chapter 4 discusses the effect of key process parameters and cover gas types on palladium distribution in Pd-Cu FABs. The grain structure and hardness of the Free Air Ball with different process parameters and cover gas types was also studied.

Chapter 5 presents a study of the mechanical properties of Cu and three types of Cu-Al IMCs namely CuAl_2 , CuAl and Cu_9Al_4 . The effect of palladium addition on the mechanical properties of the metals and IMCs will also be discussed.

Chapter 6 presents a study of the corrosion performance of Cu, Al and three types of Cu-Al IMCs namely CuAl_2 , CuAl and Cu_9Al_4 in an acidic chloride solution simulating the conditions in epoxy molded packages. In addition, the effect of palladium addition on the corrosion resistance of the samples will be evaluated.

Chapter 7 focuses on the effect of palladium distribution on the growth kinetics of Cu-Al IMCs in Pd-Cu wire bonds with thermal annealing. The interfacial morphology in Pd-Cu wire bonds will also be characterized. The results will be compared to that for bare Cu.

Chapter 8 concludes with the important findings and implications from the research work and provides recommendations for future work.

Figure 1.3 Thesis structure

1.4 Findings and Outcomes/Originality

This research led to several findings and novel outcomes by:

1. Establishing a relationship between key process parameters and the palladium distribution in Pd-Cu Free Air Ball. So far, the effect of process parameters on palladium diffusion as reported in literature has been ambiguous. Hence, there is a need to conduct the study and propose a mechanism for the diffusion of palladium in the Pd-Cu wire at different processing parameters.

2. Establishing a relationship between the hardness of Pd-Cu Free Air Ball, the palladium distribution and grain structure of the Free Air Ball. The Free Air Ball on-bonder squash measurement provides a novel method of measuring the overall Free Air Ball hardness instead of localized hardness using conventional nano-indentation method. In addition, a very thin Pd rich phase might be present at the Pd-Cu Free Air Ball periphery at certain process parameters settings, which could not be accurately measured using nano-indentation technique. The squash measurement technique serves to address the current knowledge gap on the effect of process parameters such as EFO current on the overall hardness of Pd-Cu Free Air Ball which could have an impact on bond pad damage such as pad peeling.
3. Reporting the mechanical properties such as hardness and modulus of Cu and three types of Cu-Al IMCs, namely Cu_9Al_4 , CuAl and CuAl_2 with varying concentrations of Pd which has not been published before. The study of mechanical properties of Cu-Al IMCs allows a correlation with the process responses of the Pd-Cu wire bonds at different annealing durations. The addition of palladium was observed to slightly increase the hardness and stiffness of Cu and Cu-Al IMCs.
4. Establishing a relationship between the corrosion performance of bulk Cu and Cu-Al IMCs in acidic chloride medium. This mimics the conditions in industrial molded humidity reliability tests, creating a pure environment for the corrosion test and eliminating effects from external factors such as the bond wire quality, the Al pad profile as well as the consistency of epoxy mold compounds. It allows fundamental understanding of the corrosion behavior of the individual metals, IMCs and the effect of Pd on such corrosion properties. The addition of palladium was observed to slightly improve the corrosion resistance of the metals and IMCs in the acidic chloride medium.
5. Understanding the effect of the presence of palladium at the wire bond interface on the growth rate of Cu-Al IMCs with thermal annealing. This serves to address the knowledge gap in terms of the effect of Pd distribution in Pd-Cu wire bonds on bond integrity and reliability under thermal conditions which has not been reported before.

6. Providing key operating guidelines for practicing engineers to ensure reliable Pd-Cu wire bonding.

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Chapter 2

Literature Review

Gold wire has been used in thermosonic ball bonding for many years. The continuous increase in gold prices has driven a rapid shift to copper wire and it has been widely employed in fine pitch applications in semiconductor packaging. However, bare copper wire poses some constraints as it has a short shelf-life and is readily oxidized when exposed to air. In addition, it has been reported to have poor reliability performance under humidity reliability tests. Palladium coated copper (Pd-Cu) wire has been recently adopted as an alternative to bare copper wire. The noble Pd coating is expected to limit copper oxidation. Hence Pd-Cu wire has a longer shelf life compared to bare Cu wire. In addition, Pd-Cu wire has a better stitch bond response and it is perceived to have improved corrosion resistance compared to bare Cu wire. This chapter provides a review of the literature and existing findings comparing bare Cu wire and Pd-coated Cu wire. It covers a review of the process parameters that can affect the palladium distribution in Pd-Cu Free Air Balls. The intermetallic phase transformation and growth of Cu-Al intermetallic compounds during bonding and post-annealing is also presented. This is followed by a review of Cu and Pd-Cu wire reliability studies and performances, under industrial humidity reliability and thermal cycling tests.

2.1 Palladium Distribution in Pd-Cu Free Air Ball

It is of interest to study the behavior of palladium during the Free Air Ball formation process of a Pd-Cu wire. Palladium distribution in the Free Air Ball can affect the types of IMCs formed at the bonded ball interface and the IMC phase growth, subsequently influencing the bondability and reliability. There are a few significant factors that could affect palladium distribution in Pd-Cu FAB and they are shown in Figure 2.1. 0.6 mil Pd-Cu wire FABs bonded with forming gas, were cross-sectioned and etched to study the effect of EFO current and EFO gap on Pd distribution. For a specific EFO current, the amount and distribution of Pd rich phase is similar with different EFO gaps. A more pronounced effect was seen by varying the EFO current. At low EFO current, the Pd rich phase was concentrated more at the FAB neck region. At high EFO current, the Pd rich phase was concentrated more at the FAB neck region. At high EFO current, the Pd rich phase moves to the front of the FAB and appears at the FAB tip as shown in Figure 2.2 [1].

Figure 2.1 Factors affecting palladium distribution in Pd-Cu FAB.

Figure 2.2 Palladium distributions in cross-sectioned Pd-Cu FABs as a function of EFO current and EFO gap [1].

In another study involving 0.8 mil Pd-Cu wires, palladium was seen to be concentrated near the FAB neck for FABs bonded at low EFO current. At very high EFO current, Pd was randomly distributed in swirling patterns inside the FAB as shown in Figure 2.3 [2].

Figure 2.3 Palladium distributions in Pd-Cu FAB as a function of EFO current [2].

In a study involving 0.9 mil Pd-Cu wires, ferric chloride solution was used to preferentially etch Cu, revealing Pd rich regions. No pit holes were found at the side walls of the wire bond at high EFO currents, suggesting that a Pd rich layer is formed on the FAB surface. At lower EFO currents, the etching solution attacks the thinner coating region around the tip of the FAB, resulting in pit holes [3]. A study comparing Pd-Cu wires from different wire manufacturers shows Pd rich region concentrated at the FAB neck for Pd-Cu wires from different manufacturers [4].

In a study involving different cover gas types, the use of forming gas or nitrogen was observed to have no significant influence on the Pd distribution in Pd-Cu FABs as shown in Figure 2.4 [5]. A study was performed to investigate the Pd distribution in the FAB formed between Pd-Cu wires of different Pd thicknesses, one being double of the other. It was observed that there is more Pd infusion into the Cu FAB bulk with the thicker Pd coating wire as shown in Figure 2.5. In addition, there appears to be insufficient energy at 30 mA EFO current to allow complete melting of the thick Pd coating which leads to malformed FAB formation [6].

Figure 2.4 Palladium distributions in Pd-Cu FAB with varying cover gas types [5].

Figure 2.5 Palladium distributions in Pd-Cu FAB with varying Pd coating thickness [6].

2.2 Cu-Al Interfacial Evolution during High Temperature Storage (HTS)

A common mechanism of wire bond degradation at high temperatures is the interdiffusion reaction at the bond-pad interface, which results in the excessive growth of intermetallic compound phases, causing stress built up in the pad underlying layers and

higher electrical resistance. High Temperature Storage (HTS) test is often conducted to assess wire bond strength and reliability. High temperature unmolded reliability is one major advantage for the application of Cu wire as an alternative material for low cost solution, when compared to conventional Au wire. The Cu-Al system exhibits a very slow and stable IMC phase growth and its wire bonds show less voids compared to Au-Al. The growth rate for Cu-Al IMC was reported to be 10% of that for Au-Al IMC [7]. The difference in the growth rate of IMCs was determined by the atomic properties of copper, gold and aluminum. Compared to gold atoms, copper atoms have a greater atomic size misfit in the aluminum lattice and a lower electronegativity, hence making the formation of Cu-Al IMCs more difficult [7]. Compared to the Au-Al system, which has faster diffusion of Al into Au, the Cu-Al IMC does not usually show any failure like cracks or corrosion in the un-molded conditions. The much slower growth rate of Cu-Al IMCs also implies better mechanical property and smaller increase in electrical resistance; therefore Cu-Al bonds typically have better reliability than Au-Al bonds in the unmolded condition during long service [8]. From the equilibrium phase diagram of Cu-Al system shown in Figure 2.6 [9], five IMCs, namely Cu_9Al_4 (γ_1), Cu_3Al_2 (δ), Cu_4Al_3 (ζ_2), CuAl (η_2) and CuAl_2 (θ) can be formed at temperatures below 300°C . The properties of the IMCs are listed in Table 2.1. The type of IMC formed depends on a number of factors as shown in Figure 2.7.

Figure 2.6 Phase diagram of Cu-Al system [9]

Table 2.1 Properties of Cu, Al and Cu-Al IMCs

Phase	Concentration (atm. %Cu)	Crystallographic data (unit cell, Å)	Colour	Resistivity ($\mu\Omega\text{cm}$)	Coefficient of thermal expansion (ppm/ $^{\circ}\text{C}$)	Density (g/cm^3)	Structure reference
Al	0 - 2.84	Cubic (FCC), $Fm-3m$, $a=4.049$	Silver	20 - 50	2.35	2.7	[10]
CuAl_2	31.9-33	Tetragonal ($I4/mcm$), $a=6.067$, $c=4.877$; or ($P4/mmm$), $a=4.28$,	White-yellow	7.0 - 8.0	1.61	4.36	[11,12]
CuAl	49.8 - 52.3	Monoclinic ($I12/m1$) or ($C12/m1$)	Gray	11.4	1.19	2.7	[13]
Cu_4Al_3	55.2 - 56.3	Orthorhombic ($Imm2$)	White-yellow	12.2	1.61	-	[14]
Cu_3Al_2	59.3 - 61.9	Trigonal/ rhombohedral ($P3-m1$), $a=4.106$, $c=5.094$	White-gray	13.4	1.51	-	[15]
Cu_9Al_4	62.5 - 69.0	Cubic ($P4-3m$), $a=8.7068$	White-light yellow	14.2 - 17.3	1.76	6.85	[16]
Cu	80.3 - 100	Cubic (FCC), $Fm-3m$, $a=3.615$	Red	1.7	1.66	8.93	[17]

Figure 2.7 Impact diagram showing the factors affecting IMC formation and growth.

Bare Cu bump bonded on Al pads were aged at 250°C for 64 h and three layers of IMCs were observed. The IMC phases were deduced to be Cu_9Al_4 , CuAl_2 and CuAl using micro-XRD [9]. Three IMC layers (CuAl , CuAl_2 and Cu_9Al_4) were formed after ageing bare Cu wire bonds at 205°C for 500 h. Large voids were observed which may propagate to forming cracks. The cracks grew towards the bond center interface with an increase in ageing time [18].

A study was conducted to investigate the effect of ultrasonic energy on copper bond interfacial structure. At low ultrasonic energy, a layer of native aluminum oxide occupied almost the entire bond interface and little IMC was formed. More IMC was formed at higher ultrasonic energy due to the fragmentation of native aluminum oxide [19]. CuAl_2 was initially formed after annealing bare Cu wire bonds at 175°C for 1 h as shown in Figure 2.8. After 25 h, Cu_9Al_4 was formed between CuAl_2 and the copper bond. Cu_9Al_4 and CuAl_2 grew simultaneously and Cu_9Al_4 was the dominant IMC until Al pad was depleted as shown in Figure 2.9. Subsequently, CuAl_2 was transformed to Cu_9Al_4 , with Cu_9Al_4 being the ultimate IMC. Unlike the drastic growth of voids in Au-Al bonds, only a few voids nucleated and grew adjacent to the alumina in Cu-Al bonds after annealing at 250°C for 25 h and these cavities were tens of nanometers in scale [20]. In

another study, three types of IMCs namely CuAl_2 , CuAl and Cu_9Al_4 are present at the Cu-Al bond interface after thermal annealing at 300°C for 169 min as shown in Figure 2.10 [21].

Figure 2.8 (a) TEM image of the Cu-Al interface after annealing at 175°C for 1 h; (b) lattice image and Fourier reconstructed pattern of region A-1 with CuAl_2 [001].

Figure 2.9 (a) TEM image of the Cu-Al interface after annealing at 175°C for 25 h; (b) lattice image and Fourier reconstructed pattern of region B-1 with CuAl_2 [100]; (c) lattice image and Fourier reconstructed pattern of region B-2 with Cu_9Al_4 [101].

Figure 2.10 (a) STEM image showing a tri-layer IMC; (b) line EDX showing Cu/Cu₉Al₄/alumina/Cu₉Al₄/CuAl₂/CuAl; (c) Bright Field TEM image of the same location as shown in (a); (d) lattice image and Fourier reconstructed pattern of region A in (c) with CuAl₂/amorphous alumina/Cu; (e) lattice image and Fourier reconstructed pattern of region B in (c) with CuAl; (f) lattice image and Fourier reconstructed pattern of region C in (c) with Cu₉Al₄.

Two types of IMCs, namely CuAl and Cu_9Al_4 , were present after ageing Pd-Cu wire bonds at 175°C for 1000 h, with Cu_9Al_4 formed between the Cu bond and CuAl . It was also reported that thinner aluminum remain helps to suppress the formation of overall IMC and Cu_9Al_4 [1]. TEM-EDX line scan was used to trace the Pd in the Pd-Cu bonds after annealing. In the as-bonded state, no Pd was detected in the bond interface central. An EDX line scan crossing the central interface of a bond aged at 175°C for 24 h shows that two layers of IMCs were formed and Pd was absent in the central interface. After ageing for 168 h, Pd congregated and relocated and a limited amount of Pd (2.5-3.0 at.%) was detected at the bond central as shown in Figure 2.11. A 100 nm thick Pd rich phase was also found at the bond peripheral. A 20 nm thick CuAl_2 IMC was formed in the as-bonded state where aluminum oxide was broken during bonding. Cu_9Al_4 appears as a second IMC between CuAl_2 and copper ball at the early stage of annealing. CuAl_2 and Cu_9Al_4 grew simultaneously and the former was the dominant phase until the Al pad was depleted [22]. Some nano voids was also observed at the bond interface of the Pd-Cu wire bond in the as-bonded state and after thermal annealing which was not seen in bare Cu wire as shown in Figure 2.12 [22].

Palladium was shown to have no marked effect on the growth rate of Cu-Al IMCs. Combined with the fact that there was no detectable Pd signal in the IMCs, it was concluded that Pd atoms do not participate in the interfacial reaction [23]. Bare Cu and Pd-Cu wire bonds were subjected to HTS at 175°C . It was found that the IMC growth rates of both wires are similar after 2880 h. Two layers of IMC are formed for both bare Cu and Pd-Cu wire, with Cu_9Al_4 at the Cu side and CuAl_2 at the Al side. After annealing at 250°C for 500 h, the Al pad is completely consumed. For the Pd-Cu wire, the Al pad is consumed only after 2000 h. Pd was seen to slow down the Cu-Al IMC formation [24].

Figure 2.11 Evolution of Pd at the central interface of Pd-Cu wire bonds during aging at 175°C: (a, a') as-bonded; (b, b') 24h; (c, c') 48h and (d, d') 168h. EDX line scans from Al pad to Cu ball.

Figure 2.12 Comparison of voids in bare Cu (a, a' and a'') and Pd-Cu wire bonds (b, b' and b'').

2.3 Molded Humidity Reliability of Bare Cu and Pd-Cu Wire Bonds

Long term reliability of Cu wire is a major concern in replacing Au wires. There are a number of factors affecting wire bond reliability as shown in Figure 2.13. One of the most critical tests is humidity reliability test and bare Cu wire has been reported to fail humidity tests [25, 26]. The purpose of subjecting the wire bonded devices to high humidity in accelerated tests is to ensure that the devices and packages can withstand an uncontrolled, moisture-laden environment for an extended period of time, perhaps as long as their operating lifetime. Corrosion is the primary cause of failure with these types of tests. There is a variety of accelerated testing for estimating the combined effect of temperature and humidity. Regular humidity tests are the pressure cooker test (PCT) and highly accelerated temperature and humidity stress test (HAST). PCT is an ageing test under saturated pressurized vapor, so-called autoclave testing. A standard test condition of PCT is 121°C – 100% RH (relative humidity). HAST test is usually carried out at 130°C – 85% RH in either biased or unbiased mode. The biased mode is a stricter humidity test since it further accelerates the failure of the wire bonds [27]. Under high

humidity conditions, substrate based packages will experience a higher failure rate compared to lead frame packages. This is due to the high moisture absorption and halogen content in substrate packages which increase corrosion [28].

Mold compound protects the device mechanically and environmentally from the outside environment. Transfer molding compound is used to encapsulate most wire bonded packages as illustrated in Figure 2.14. Two types of epoxy mold compounds (EMC) are typically used to encapsulate the bonded samples. One is conventional EMC containing bromine (Br). The other is a green resin without flame retardant such as Br. Chloride (Cl) is a typical impurity present in all the epoxy molds and different Cl ion content can be prepared by applying a different purification level of epoxy resin. It was found that halogen speeded up corrosion of copper wire bonds and caused open failures at early stage of PCT. Chloride ions exist in epoxy mold compounds and should be kept as low as possible. Failures are considered to have occurred if the channels show a resistance increase of more than 20% [30].

Figure 2.13 Impact diagram showing factors affecting wire bond reliability.

Figure 2.14 Schematic of a wire bonded device encapsulated in mold compound [29].

Bare Cu wire showed better HAST response in EMC with low chloride content compared to EMC with high chloride content. With high chloride content EMC, a corrosion layer was observed between Cu and CuAl_2 IMC. Al, O and Cl elements were observed at the corrosion layer. Cu_9Al_4 was postulated to be the intermetallic phase that has corroded. A low pH in the EMC was also shown to accelerate the corrosion and give poor reliability performance [31]. Green EMC and green substrate are essential for high reliability performance under humid conditions. Bare Cu wire bonds encapsulated in green EMC passed humidity tests whereas those encapsulated in non-green substrates experienced open failures under 96 h unbiased HAST test. Chloride was detected in the vicinity of the failure [25]. Bare Cu bonds were subjected to High Humidity High Temperature Reverse Bias (JEDEC22 A-101) tests. CuAl_2 layer was formed next to the Al while CuAl and Cu_9Al_4 IMCs were identified close to the Cu ball in a wire bond after high temperature storage. With humidity reliability test, corrosion effects preferentially took place in the Cu rich IMCs, CuAl and Cu_9Al_4 while the CuAl_2 IMC remained stable [32].

Pd-Cu wire was perceived to give enhanced reliability compared to bare copper wire under PCT and unbiased HAST. The lifetime for Pd-Cu and bare Cu wire bonds were over 800 h and 250 h respectively and the type of EMC used (Conventional or green EMC) has no influence on the wire bond reliability. For Pd-Cu wire, uniform IMC growth was observed at the bond interface, with no cracks or voids formed. Pd enriched layers was observed to control the interdiffusion of Cu and Al atoms, and retards certain corrosive copper IMC from forming. Continuous cracks were found at the bond interface

for bare Cu wire. Chloride was detected at the failure vicinity with green EMC while bromide was detected at the failure vicinity with conventional EMC. It was presumed that the predominant IMC before corrosion would be Cu_9Al_4 [33].

For the green EMC, Cl^- moves into the gap of the bonding interface and attacks Cu_9Al_4 . Uno postulated that Cu_9Al_4 is corroded by Cl^- and produces Al oxide (Al_2O_3). The postulated reactions are as described below:

In another biased HAST test, bare Cu and Pd-Cu wires showed good reliability performance for low Cl and high pH molding resin. For the conventional EMC containing Br, Pd-Cu wire bond could withstand up to 380 h. PCT test conducted on bare Cu and Pd-Cu wire bonds in unmolded conditions showed no degradation up to test end at 384 h [2]. However in another reliability study involving bond pad of various finish, it was observed that the ball pull test (BPT) value for Pd-Cu wire on Al pad without molding decreased significantly after 528 h of unbiased HAST as shown in Figure 2.15. A micro crack was observed at the copper-aluminum interface as shown in Figure 2.16. Conventional EMC containing Br was then compared with green EMC. With conventional EMC, the average BPT value decreased significantly with large amount of ball lifts occurrence after 528 h unbiased HAST. The BPT value decreased slightly with green EMC as shown in Table 2.2. It was observed that EMC containing Br speeds up the corrosion between copper and aluminum markedly [34].

Figure 2.15 Ball pull value plot at various unbiased HAST durations of Pd-Cu wire bonds bonded on different pad finish [34].

Figure 2.16 Micro crack observed at the Pd-Cu bond interface after unbiased HAST [34].

Table 2.2 Average ball pull test values with different EMCs [34]

EMC	Average BPT value (g)		
	144hrs	336hrs	528hrs
Green (without bromine)	8.6	8.0	6.4
Halogen (with bromine)	6.3	5.1	2.3

Two IMC layers, namely Cu_9Al_4 and CuAl_2 , were observed after HTS at 175°C for 2880 h. For bare Cu wire with green EMC, open failures occurred after 500 h of PCT testing. Cu_9Al_4 layer was observed to disappear and it was replaced by a narrow gap and CuAl layer. CuAl_2 was the only remaining IMC. The narrow gap was presumed to be due to the corrosion of Cu_9Al_4 . Cl was detected in the vicinity of the crack. For Pd-Cu wire, after 1000 h of PCT, Cu_9Al_4 and CuAl_2 were still detected at the interface. No crack can be seen and it was deduced that the presence of Pd can result in the formation of corrosion resistant IMC [24].

The effects of pH levels and Cl content in the EMC and substrate halogen content on reliability was investigated using Pd-Cu wire. The pH content was modified with ion-catcher systems. After 2000 h of HTS, no failure was observed in different EMCs and substrates, even for components using EMC with the most severe pH/Cl⁻ combinations. CuAl_2 and Cu_9Al_4 were found at the cross-sectioned interface after 100 h of HTS. For the biased HAST test, negative channels were not as rapidly corroded as the positive channels suggesting the rate of corrosion is accelerated by the diffusion of negatively charged ions towards the positive channels forming an acidic environment. Higher failure rate was observed for components using high halogen content substrate at 192 h

compared to a substrate with low halogen content. Cl^- was detected at the failure vicinity. Low pH in the molding compound was observed to accelerate corrosion at the bond interface by selectively etching away the Cu_9Al_4 layer, creating a self-propagating crack between Cu and CuAl_2 IMC layers. The halogen content of the substrate was observed to make a significant difference in the performance of HAST tests [30]. Cu_9Al_4 was not present after biased HAST test and was presumed to be consumed in the test with a hypothesized process:

2.4 Thermal Cycling Tests of Bare Cu and Pd-Cu Wire Bonds

Thermal cycling can result in flexure failure due to differences in thermal expansion of packaging materials such as the substrate, die, wire bonds and mold compound. Due to coefficient of thermal expansion (CTE) mismatch between the Cu wire (17 ppm/°C), Al pad (24 ppm/°C) and Si die (3 ppm/°C), the bond pad interface is under stress during temperature cycles [28]. In addition, interfacial Cu-Al IMC continues to grow under temperature cycling and micro cracks may occur at the bond interface [28]. 1.0 mil bare Cu and Pd-Cu wire bonds were subjected to thermal cycling tests from -65°C to 150°C for 10000 cycles. Pd-Cu wire bonds were shown to have zero failure compared to bare Cu wire bonds with 91% failure rate [35]. Gan et al. [36] compared the thermal cycling reliability of 0.8 mil Pd-Cu wire with 4N Au wire under a thermal cycling profile from -40°C to 150°C. Pd-Cu wire bonds exhibited better thermal cycling performance than Au. Small outline transistor devices connected with 0.8 mil Cu wire and encapsulated with commercial EMC were subjected to thermal cycling tests from -50°C to 150°C at a ramp rate of 20°C /min. The cycle duration was 30 min. No voids or

cracks were observed up to 1500 cycles of the test. In addition, all the SOT devices passed the electrical resistance test. This was attributed to the slow Cu-Al IMC growth rate [37].

2.5 Summary and Remarks

From the review of different literatures published from previous studies, it was shown that EFO current is the dominating factor affecting Pd diffusion in Pd-Cu FAB during FAB formation. The use of forming gas as an inert gas was also shown to result in less malformed ball formation compared to using nitrogen gas. As a result, forming gas is more commonly used as a shielding gas for Pd-Cu wire bonding in packaging companies. It is apparent that palladium addition can have an effect on the Cu-Al intermetallics growth and phase formation. Palladium addition would also influence the bondability and reliability of the copper wire bonds especially in molded humidity reliability tests, where the chloride ion from the epoxy mold compound interacts with the Cu-Al IMC, causing it to corrode. So far, based on literature there has been conflicting results on whether palladium helps to improve the performance of Cu wire bonds in humidity reliability test. In addition, no literature has been reported on whether it is crucial for Pd to be present at the bond interface of Pd-Cu wire bonds to affect bondability and reliability of the bonds. Hence, it is of particular interest in this project to study the effect of palladium distribution on bondability, Cu-Al intermetallic formation and growth, and reliability.

This project started with investigating the effect of Free Air Ball (FAB) formation parameters such as the electronic flame off (EFO) current on the palladium distribution in the FAB. Pd-Cu wire bonds with different palladium distribution are produced. 1) Presence of Pd at the wire bond interface; 2) absence of Pd at the wire bond interface (i.e. Pd is expelled elsewhere during the ball formation). Bare Cu wire bonds are used as a reference. The effect of palladium distribution on the hardness of Pd-Cu FABs and its bondability will also be studied. A novel FAB squash measurement technique was used to obtain the overall hardness of the FAB before impacting on the Al bond pad.

With thermal annealing, the thickness of Cu-Al IMCs will increase and different Cu-Al IMCs would be formed at various annealing durations. In what follows, the mechanical properties such as hardness and stiffness of the individual Cu-Al intermetallics with the addition of Pd were studied by employing nano-indentation techniques. The mechanical properties of the individual Cu-Al IMCs has not been published before in literature. Hence mechanical data of the individual IMCs such as hardness and stiffness would be beneficial to correlate to the process bonding response during thermal annealing. Lastly, an electrochemical test was conducted to study the effect of Pd addition on the corrosion performance of individual Cu-Al IMCs in an acidic chloride medium. The setup serves to create a pure environment, mimicking the conditions found in commercially available epoxy mold compounds and eliminating effects from external factors such as wire bonding parameters, epoxy mold compound consistency and Al pad profile. These tests enable us to understand the fundamental behavior of Pd-Cu wire bonds during high temperature storage test and humidity reliability test. The work will answer a few challenging questions, viz: 1) the effect of thermal annealing on the hardness and bondability of Pd-Cu wire bonds at different annealing durations. 2) Does Pd help to improve the corrosion resistance of the wire bonds and Cu-Al intermetallics in molded humidity reliability test? 3) The Cu-Al IMC that is most susceptible to corrosion by chloride ions, and predicting the failure of Pd-Cu wire bonds during humidity reliability test.

The answers to these questions are fundamental in materials science, and also bear significant implication to the long-term reliability of electronic packages and devices.

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Chapter 3

Experimental Methodology

This chapter provides a detailed description of the equipment setup, materials, sample preparation procedures, and characterization and analysis techniques. The rationale of using certain techniques and the operating principles of the equipment are discussed.

3.1 Synthesis of Wire Bonds

3.1.1 Bonding Equipment and Materials

A Kulicke and Soffa (K&S) IConn ProCu^{PS} automatic ball bonder was employed for thermosonic copper ball bonding as shown in Figure 3.1. An inert cover gas system was used to prevent oxidation of the molten wire during the ball formation process.

Figure 3.1 K&S IConn ProCu^{PS} automatic ball bonder.

A Kulicke and Soffa (K&S) capillary with a granular finish was used for the copper ball bonding as shown in Figure 3.2 and the capillary dimensions provided in Table 3.1.

Figure 3.2 Capillary tip geometry dimensions (tip diameter (T), hole diameter (H), chamfer diameter (B), inside chamfer (IC), inside chamfer angle (IC angle), and outside radius (OR))

Table 3.1 Capillary dimensions

H, μm	CD, μm	FA, $^\circ$	T, μm	OR, μm
18	22	8	50	7

A 15 μm 4N bare copper wire (Heraeus) and Pd-Cu wire (Nippon Micro metal Corporation) with a Pd layer thickness of around 70 nm was used for the thermosonic bonding. The main properties of the wires are listed in Table 3.2.

Table 3.2 Bare Cu and Pd-Cu wire properties

Properties	Pd-Cu	Bare Cu
Wire diameter, μm	15	15
Composition, wt%	99.99 Cu core. 2.8 wt.% Pd	99.99
Breaking load, g	4.13	3.82
Elongation, %	9.17	11.32

Thick aluminum pads of 1 μm thickness with a bond pad pitch of 60 μm were employed in this study (Figure 3.3). A SiO_2 film between the Al pads and Si is insulation.

Figure 3.3 Image of Al pad (a) Top view and (b) Cross-sectioned view.

3.1.2 Ball Bonding Process

The bonding wire was fed through an air guide, tensioner, wire clamp, capillary and bonded off. The end of the wire was then sparked with an electronic flame off (EFO) to produce a spherical free air ball (FAB) at the wire tip. The free air ball is formed by the effects of surface tension while exposing to a high voltage and low current spark of an electric flame off. Under the high temperature environment, the copper FAB is easily oxidized which leads to inconsistency in ball shape and size making it difficult to control bonding parameters. Robust copper kit was installed to provide an inert environment for the free air ball formation process. The kit comprised of gas nozzles fitted around the

electronic flame off electrode to cover the spark region with forming gas. Forming gas (95% N₂ + 5% H₂) was employed to prevent oxidation of the FAB during ball formation process. Oxidation can occur if the cover gas flow rate is not sufficiently high to provide an inert atmosphere for the FAB formation. Too high forming gas flow rate will lead to small balls or pointed balls due to the cooling effect from the gas [1]. Hence, the forming gas flow rate was set at 0.5 L/min as recommended by the manufacturer [2].

The FAB formed during the EFO process was transferred onto the bond pad to form the copper first bond by a combination of normal bonding force, ultrasonic vibration and heat. A whole bonding duration consists of three basic stages: (i) standby stage, (ii) contact stage and (iii) bonding stage. A standby stage is the initial stage when the free air ball is touched on the bond pad. During the contact stage, a high bonding force and low ultrasonic power are usually employed to give initial deformation of the FAB. During the bonding stage, a low force and high ultrasonic energy are used to ensure good adhesion of the bond with the bond pad, to ensure robust bonds. The ultrasonic vibrations fragment the native oxide layer on the Al bond pad. Metal interdiffusion and IMC formation takes place during the latter stage, so the bonding strength is mainly determined by the bonding stage.

The bonded samples were immediately removed from the heated workholder after bonding to reduce post thermal effects on interfacial reactions. However, it is inevitable that the device maintained a temperature near 175°C for ~5sec. The whole bonding cycle is illustrated in Figure 1.1.

3.1.3 Ultrasonic Energy

Ultrasonic energy (USG) determines the bond strength and reliability of the wire bonds. Ultrasonic vibration under certain pressure and heat partially fragments the native alumina layer (~10 nm thick) on the aluminum bond pad, providing the pathways for Cu-Al interdiffusion. This promotes the formation of the intermetallic compounds (IMCs) and consequently improves the bonding strength significantly. At very low USG levels, non-stick on pads (NSOPs) or ball lift can occur during ball pull test. At very high USG levels, pad damage such as pad peels is encountered for copper bonding. Excessive USG

can also cause squashed bonds, cracks and cratering to the underlying pad structure [3]. Hence the USG has to be optimized.

3.1.4. Bond Force

The bond force is the downward force exerted by the bonding head during bonding. The USG is optimized along with the bond force. The bond force is the primary parameter that controls the bonded ball diameter and height. A high bond force transmits high force onto the bond pads, which is not desirable, since it can cause pad damage such as pad cratering and squashed balls. A low bond force can lead to non-stick on pad (NSOP) and ball lifts condition. Hence the bond force has to be optimized properly.

3.1.5. Bond Time

Bond time is the duration of the application of USG and force. Excessive bond time results in low throughput, increased contaminants built up on the bond tool, causing the bond tool to be worn out faster. Shorter bonding times are preferred for higher unit throughput in industrial applications. However, very short bond times may result in ball lifts. Hence the bond time has to be optimized together with the bond force and USG.

3.2 Preparation of Samples

3.2.1 Synthesis of Bulk Metal and Cu-Al Alloys

Bulk Cu metal alloys were synthesized to mimic the conditions at the Pd-Cu wire bond interface where varying concentrations of Pd could be present by adjustment of the EFO current. Various Cu-Al IMCs were synthesized to mimic the conditions at the Pd-Cu wire bond interface during thermal annealing where different Cu-Al IMCs could be formed between the Cu bond and Al bond pad. Mechanical and electrochemical properties of the individual metal alloys and Cu-Al IMCs are thereafter studied. Elemental Cu, Al and Pd with 99.95% purity were commercially obtained from Sigma-Aldrich. The metal and intermetallic bulk alloys ingots were prepared using an arc melter

in an argon gas environment as shown in Figure 3.4. The arc melter was selected for preparation of the bulk alloys because it can produce temperatures in excess of 2000°C and can be used to melt metals up to 3500°C [4]. In the arc melter, an electrical arc is used to melt the metals for making an alloy. The arc-melter consists of two key components: (i) a hearth with crucibles of one electrical polarity and (ii) electrode of opposite polarity. Elements to be melted are placed in one of the crucible of the hearth and electrode is used to strike the arc to melt the materials. The air inside the arc melter is first purged by a mechanical pump, followed by backfilling with inert argon gas. Evacuation of the arc melter eliminates oxidation of the metal samples during melting. A suitable current is then set in the power supply. A higher current is used for materials with higher melting temperatures. First the electrode is used to strike the tungsten to create an electrical arc. Then the heat generated from electric arc is used to melt the metal material under the continuous flow of argon gas. The electrode is moved around and over the material in order to ensure a uniform and homogeneous melt. The metal ingot is turned over and re-melted several times to ensure good homogeneity of the samples. The melting-solidification-turnover of sample- re-melting process is typically repeated for six times to attain compositional homogeneity. The synthesis process is shown in Figure 3.5.

Figure 3.4 Diagram of (a) Arc melter and (b) Arc melter chamber.

Figure 3.5 Synthesis process of metals and intermetallics ingots.

3.2.2 Isothermal Annealing

Isothermal annealing was performed on the wire bonds to simulate the conditions of the device service, so as to investigate the interfacial evolution and its effect on failure of the bonds. The bare Cu and Pd-Cu wire bonded samples were annealed at 175°C in an oven flowed in with nitrogen gas. The nitrogen gas provides an inert environment and minimizes oxidation of the samples. The temperature control accuracy of the oven is $\pm 2^\circ\text{C}$; durations of annealing were 24, 48 and 168 hours.

3.3 Process Response Measurements

3.3.1 Measurements of Bond Geometry

The geometry of ball bonds is defined by two parameters- ball diameter and the ball height. The ball diameter, $D = (D_x + D_y)/2$, where D_x and D_y are the diameters of the bonded ball perpendicular and along the direction of the ultrasonic vibration, respectively, as illustrated in Figure 3.6a. The ball height is the distance between the bond pad and the edge of the bonded ball as shown in Figure 3.6b. The values of ball diameter and ball height were recorded using Nikon MM-400 optical microscope shown in Figure 3.7. 20 bonded balls were measured for each condition and setting.

Figure 3.6 Geometry of a bond: (a) Bonded ball diameter and (b) Bonded ball height.

Figure 3.7 A Nikon MM-400 measuring microscope.

3.3.2. Shear Tests

The shear tests were performed with a DAGE 4000 micro-tester at a shear height of $3\text{ }\mu\text{m}$ and a tool movement speed of $4\text{ }\mu\text{m/s}$ (Figures 3.8 and 3.9). The load that causes fracture of the bonds is called shear force. 20 samples were measured for every condition. The shear per area (SPA) is calculated by dividing the measured shear force (SF) by the

area of the bonded ball. The equation is:

$$SPA = \left(\frac{SF}{\frac{\pi}{4} \times D^2} \right) \quad (3.1)$$

Figure 3.8 Illustration of the shear test.

Figure 3.9 A DAGE 4000 micro-tester.

3.3.3. Pull Test

The pull tests were performed with a DAGE 4000 micro-tester with a pull test cartridge. 20 samples were measured for each condition. First bond pull was performed at

the top of loop near the ball neck.

3.3.4. IMC Coverage and Al Splash Measurement

After post bonding, the IMC between an Al pad and copper bond is very thin and cannot be observed optically. In order to compare the differences in IMC coverage between Pd-Cu and bare Cu wire bonds, the device was annealed for some period of time to allow the IMC to grow as shown in Figure 3.10. A 4 hours baking at 175°C is used followed by etching with a 50 wt. % concentration nitric acid. The etching procedure is described below [3]:

1. Bake the sample at 175°C for 4 hours.
2. Etch the sample with 50 wt.% nitric acid at room temperature for 50 seconds.
3. Rinse the device with deionized water.
4. Rinse again with deionized water in an ultrasonic cleaner for about 2 minutes.
5. Rinse the device with ethanol.
6. Thoroughly blow dry with air.

The IMC coverage on the bond pad is calculated by the percentage of IMC area out of the total contact area as shown in equation 3.2 [1]. The IMC coverage is calculated by Kulicke & Soffa in-house developed software based on visual contrast. An example of the IMC analysis is shown in Figure 3.11, where the contact area is enclosed by the green color line and the non-IMC areas enclosed by the red line.

$$IMC\% = \frac{IMC\ Area}{Contact\ Area} \quad (3.2)$$

The splash is measured on the bond pad in the USG application direction after etching the bond as shown in Figure 3.12. The splash is measured to ensure that the splash is within the bond pad area as Al splash out can cause passivation cracking and reliability failures of the device.

Figure 3.10 IMC coverage of a sample after annealing at 175°C for 4 hours.

Figure 3.11 Analysis of the IMC coverage.

Splash
Measurement after
etching away the
ball

Figure 3.12 Splash measurement.

3.4 Materials Characterization

3.4.1 Electron Backscatter Diffraction

The grain structure such as the grain size and grain orientation of the cross-sectioned FABs was determined in-situ using EDAX Digiview IV Electron Backscattered Diffraction (EBSD) detector attached to the dual-beam Focused Ion Beam (FIB) system. The EDAX Orientation Imaging Microscopy (OIM) version 6.2 software was used for grain size and grain orientation analysis. The surface finish of the analysis area has a large impact on the quality of the obtained diffraction patterns and the accuracy of the subsequent indexing. This requires a bulk sample with a flat surface and a surface free from preparation induced deformation and oxidation [5]. Since sample surface finish is important for EBSD analysis, focused ion beam was used for cross-sectioning the samples before analyzing the grain structure with an EBSD detector. Sample preparation in-situ under vacuum prevents oxidation of the samples which will degrade the observation. The accelerating voltage of the primary electron beam within the SEM is typically set to 20 keV for an EBSD analysis. The specimen is positioned within the SEM sample chamber such that a small angle, typically 20 degrees, is made between the incident electron beam and the specimen surface. The specimen is thus tilted to a high angle of 70 degrees with respect to the horizontal axis. This high tilt angle enhances the proportion of backscattered electrons able to undergo diffraction and escape from the specimen surface [6]. A schematic of the setup is shown in Figure 3.13.

Figure 3.13 Schematic illustration of an EBSD setup and sample arrangement in the SEM [7].

When the primary beam interacts with the crystal lattice, low energy loss backscatter electrons are channeled and are subjected to path differences that lead to both constructive and destructive interferences. Some of the electrons are incident on atomic planes at angles that satisfy the constructive interference condition of Bragg's law [7]:

$$n\lambda = 2d \sin \theta \quad (3.3)$$

where d = perpendicular distance between two diffracting planes

θ = angle between the incident electron beam and the diffracting planes

λ = wavelength of the electrons

n = an integer

When Bragg's Law is satisfied, these electrons are diffracted and if a phosphor screen is positioned in the path of the diffracted electrons, a short distance from the tilted sample, a diffraction pattern can be observed. The diffraction pattern produced on the phosphor screen contains characteristic Kikuchi bands which are formed where the regions of enhanced electron intensity intersect the screen (Figure 3.14).

Figure 3.14 Example of Kikuchi lines [8].

The diffraction pattern is characteristic of the crystal structure and orientation in the sample region where it was generated. Each Kikuchi line represents a crystallographic plane (hkl) and the band width is proportional to the inter-planar spacing d_{hkl} of plane

(hkl). The zone axis is located at the intersection center of the bands with the axis direction perpendicular to the pattern surface. Hough transform is used to identify the positions of the Kikuchi bands. It converts the image from the EBSD camera into a representation in Hough space, by using the following relation between the points (x, y) in the diffraction pattern and the coordinates (ρ, θ) of the Hough space as shown in equation 3.4 [7]:

$$\rho = x \cos \theta + y \sin \theta \quad (3.4)$$

A straight line in the image space (x, y) can be characterized by ρ , the perpendicular distance from the line to origin and θ , the angle made with the x -axis, and can be represented by a single point (ρ, θ) in Hough space. Thus a number of points belonging to one line in (x, y) space will be represented as a number of lines in (ρ, θ) space passing through a single point. The Kikuchi lines appear as bright regions or peaks in Hough space, which are easily detected and used to index the diffraction pattern as shown in Figure 3.15.

Figure 3.15 (a) Diffraction pattern (b) Peaks in Hough transform (c) The bands in the diffraction pattern corresponding to peaks in Hough space (d) The indexed diffraction pattern [8].

The grain orientation is recorded using the Euler (Euler 1775) angle convention. Three Euler angles describe a minimum set of rotations that can bring one orientation into coincidence with another. During a measurement, this is the relationship between the EBSD detector and the particular point on the sample being measured under the beam. The grain size can be calculated by using differences in crystallographic orientation between surrounding grid points of greater than a defined minimum, typically 10 degrees, to obtain the position of grain boundaries. The exact location and characteristics of each grain boundary can be identified since the phase and orientation is known at each indexed point. With the grain boundaries and phase information obtained, the grain size distribution within the sample can be calculated.

3.4.2 On-bonder Hardness Measurement

The hardness of the Pd-Cu and Cu FABs was measured using an on-bonder squash measurement technique [9]. This technique was used as it is able to provide a hardness index of the overall FAB based on the amount of squash instead of the usual hardness measurement such as nano-indentation, where specific indents are made. Palladium rich phase might be present at the peripheral of the FAB as a thin layer, making measurement with nano-indentation difficult. The amount of squash is measured during a time period where the bonding force is applied. The incremental z-axis squash movement is recorded by the z-axis encoder in encoder counts and subsequently converted to a hardness index.

3.4.3 X-Ray Diffraction

The crystal structure of the bulk metals and Cu-Al alloys with varying concentrations of Pd was identified using a Shimadzu 6000 X-ray diffractometer (XRD) and Cu K α radiation (wavelength 1.5418 Å) at 40 kV and 30 mA. XRD was employed as it is able to identify the exact phase formation by matching the experimental diffraction peaks of the bulk samples with the theoretical peaks. XRD was used to identify the intermetallic phases formed in the joints between Al and Cu bars fabricated by friction welding [10]. Cu K α radiation is used due to its short wavelength. As a result, it can be

used to detect smaller crystal plane spacing. Figure 3.16 illustrates the geometrical arrangement of the X-ray source, sample and the detector. A parallel beam of X-ray waves incident on a crystal will be diffracted if and when the constructive interference conditions are satisfied. These conditions are contained within Bragg's Law which states that [7]:

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \quad (3.5)$$

where d_{hkl} = perpendicular distance between two crystal planes

θ_{hkl} = angle between the incident beam and the planes

λ = wavelength of the incident X-ray beam

n = an integer

A schematic of the interference of waves is shown in Figure 3.17. From Bragg's law, the hkl diffraction peaks occurs at the measured angle $2\theta_{hkl}$. Each distinct peak corresponds to an individual inter-planar spacing, d . An example of diffraction peaks is illustrated in Figure 3.18. For a cubic sample,

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \quad (3.6)$$

where a = lattice parameter and

h, k, l = Miller indices.

Combining the equations, we have

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \quad (3.7)$$

By using X-rays of known wavelength λ and measuring θ , the spacing d of various planes in a crystal can be determined. By continuously changing the incident angle of the X-ray beam, a spectrum of diffraction intensity vs the angle between incident and diffraction beam is recorded. Relative movements among the X-ray tube, specimen surface and the detector ensure the recording of diffraction intensity in a range of 2θ . A Bragg-Brentano diffractometer arrangement is used in which the X-ray incident beam is fixed but the sample stage rotates around in order to change the incident angle. The

detector also rotates and its angular speed is twice that of the sample stage in order to maintain the angular correlation of θ - 2θ between the sample and the detector rotation.

The positions and intensities of the peaks in the observed diffraction pattern are matched with a known pattern of peaks from a standard sample from the International Centre for Diffraction Data (ICDD) database using the Match! software version 2.33. Hence the directions in which an incident beam is being diffracted by a given set of lattice planes is determined by the crystal system to which the crystal belongs and its lattice parameters. This allows the diffraction peaks obtained to be indexed.

Figure 3.16 Arrangement of an X-ray diffractometer [11].

Figure 3.17 Geometry for the interference of a wave scattered from two planes separated by spacing, d [11].

Figure 3.18 Example of an indexed diffraction pattern [11].

Phase quantification of multi-phase specimen was carried out by Rietveld refinement using the software Topas Academic version 4.1. Rietveld refinement is a technique devised for use in the quantitative analysis of multiple phases in a specimen. In Rietveld refinement, the intensity profile is fitted to structural models using a least square calculation. The calculated intensity is based on the crystallographic structures and XRD instrumental parameters. The background was fitted using a 7th order Chebyshev polynomial function. Quantitative analysis is based on the correlation between the intensity of the diffraction peaks of a particular phase in a multi-phase specimen and the concentration of that phase in the mixture.

3.4.4 Nano-indentation

The indentation tests of the bulk metals and Cu-Al alloys were performed with a MTS Nanoindenter XP® system using a Continuous Stiffness Measurement (CSM) technique [12]. This technique was introduced by Oliver and Pharr in 1992. In conventional nanoindentation measurement, the indenter is driven into the sample by a fixed load and the material stiffness measured from the unloading cycle of the curve. Using the CSM technique, during loading, a small oscillatory force with a frequency of 45 Hz and amplitude of 2 nm was imposed on the nominal load to extract contact stiffness (S) as a continuous function of the indenter's displacement into the sample as shown in Figure 3.19. The amplitude of the force oscillation is kept sufficiently small so

that the deformation process is not significantly affected by its addition. The CSM method offers many advantages over the conventional method such as:

1. It can provide continuous results for contact stiffness as a function of depth.
2. It allows significant time savings in calibration and testing. As the data is only extracted from a single loading/unloading cycle, there is no need for multiple unloading.
3. The CSM is employed at high frequencies, thus eliminating time dependent plasticity and thermal drift during the experiment.
4. It allows measurement of the effects of stiffness changes as well as damping changes at the point of initial contact.

Figure 3.19 Schematic of the CSM loading cycle [13].

The tests were performed using a Berkovich tip. The Berkovich tip is a three-faced pyramid with a radius around 50 nm at the apex. The indenter was pressed into the materials at a constant strain rate of 0.05s^{-1} . The maximum depth approached into all samples was 2000 nm. Ten indentation points at different locations were made for each of the samples. The reported modulus and hardness were extracted from the loading process as the average values in the depth range from 1600 to 1800 nm. At this depth range, the modulus and hardness values were stabilized. The hardness and stiffness can be calculated from the following expressions as described in [12].

The hardness (H) is expressed in the form:

$$H = \frac{P}{A_{\max}} \quad (3.8)$$

where P is the indenter load and $A_{\max}$ is the maximum projected area into the sample.

The reduced modulus E_r can be obtained from the contact stiffness, S by the following expression:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_{\max}}} \quad (3.9)$$

where S , the contact stiffness is a function of:

$$S = S(f, a, \Phi, m, K_s, K_f) \quad (3.10)$$

where f is the oscillation frequency; a is the amplitude; Φ is the phase angle between the force and displacement signals; m is the mass of the indenter; K_s is the spring constant and K_f is the frame stiffness.

The reduced modulus E_r is also expressed in terms of the elastic moduli (E) and Poisson's ratio (ν) of the specimen, E_i and ν_i are the parameters for the indenter:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (3.11)$$

Continuous modulus (E) and hardness (H) profiles can thus be calculated with respect of indentation depth from equations (3-8) to (3-11) with a single loading/ unloading cycle.

3.4.5 Electrochemical Test

A three electrode cell configuration is being used for the electrochemical test of the arc-melted metals and IMC alloys samples. The three electrodes, namely counter, reference and working electrode are immersed in an acidic chloride medium and connected to a potentiostat. The setup of the electrochemical cell is shown in Figure 3.20. The potentiostat allows the potential difference between the reference and working electrode to be controlled with minimal interference from IR (ohmic drop). In this configuration, the current flowing through the reference electrode also can be minimized thereby avoiding polarization of the reference electrode and hence keeping the applied potential distribution between the working and reference electrode stable. The reference electrode is positioned close to the working electrode to minimize the IR drop due to the

resistivity of the solution phase. The electrodes consist of the following:

1. Reference electrode: A Ag/AgCl electrode
2. Counter electrode: Non-reactive high surface area electrode. In this case platinum was used.
3. Working electrode: Metal and IMC samples.

Figure 3.20 Setup of the electrochemical cell.

The reference electrode provides a fixed reference potential against which the potential of the working electrode is measured. The half-cell reactions utilized in this electrode are given in the equation:

Working electrode is the electrode which is studied. The counter electrode is the electrode in the cell that completes the current path. Gamry software PHE200TM (Gamry Instruments) is used to record the currents and potentials.

3.4.6 TEM Sample Preparation

A FEI Nova 600 Nanolab dual beam focused ion beam (Figure 3.21) was utilized to prepare region-specific SEM and TEM samples at the Cu-Al interfacial regions. As

compared with traditional preparation methods such as mechanical polishing and ion beam etching, the dual beam is suitable for locating a specific region, making it especially suitable for multi-interface observation in high resolution analysis. The FEI Nova 600 Nanolab is a dual-beam instrument that integrates ion and electron beam for FIB and SEM functionality in one machine. The electron beam and ion beam are placed in fixed position, with a 52° angle between them for optimal performance as shown in Figure 3.22. A working distance of 5 mm was used for the FIB set up. Convergence of the SEM and FIB at a short working distance allows precision milling, etching, deposition and analysis at high resolution.

The main procedures of TEM sample preparation of the copper wire bonds using FIB in this study are shown in Figure 3.23. First, the wire at the top of loop is milled off using the highest ion beam current. Then two trenches are opened up by ion beam, leaving an approximate 5 μm wide foil between them. The foil is then milled at the top by the bombardment of ion beam to a height of approximately 4 μm to the ball/ pad interface. This is followed by cleaning of the cross section using a scanning ion beam with a low beam current. The cross-section is ready for in situ SEM observation. Image analyzer software, Image J (Version 1.49), was utilized to measure the area of the entire IMC layer from SEM images and a nominal thickness was obtained by dividing the IMC area by the ball diameter.

For TEM sample preparation, the prepared 5 μm foil is further thinned to approximately 1.5 μm using a cleaning cross section process and followed by a U-cut. An omniprobe in situ tungsten lift out probe is used to hold the region-specific TEM foil. The omniprobe is attached to the foil by ion beam assisted Pt deposition. The TEM foil is then cut off from the sample and lifted from the bulk sample using the omniprobe. A semicircular Mo TEM grid is positioned on the sample stud for supporting the TEM sample. A Mo grid is used instead of a Cu grid to avoid EDX peaks overlaps since the samples are Cu wire bonds samples. After lifting out the TEM foil, the grid is moved into the field of view. The omniprobe is lowered until the foil touches the Mo grid. The specimen is then attached to the TEM Mo grid using Pt deposition. The tungsten probe is then milled free by the ion beam. A scanning ion beam with low current (0.28 nA and below) is then used to attenuate the specimen to electron transparency (~ 50 nm). Lastly, a

low voltage ion beam (89 pA, 2 kV) is employed to clean the surfaces of the TEM foil to remove amorphous regions caused by the ion beam bombardment.

Figure 3.21 FEI Nova 600 Nanolab FIB.

Figure 3.22 Schematic diagram showing the configuration of a dual-beam focused ion beam system [14].

Figure 3.23 Procedures for SEM observation and TEM sample preparation using FIB: (a) Wire loop chopped off from the ball bond. (b) two trenches are milled to produce an approximately 5 μm wide foil (c) Foil is further milled off at the top to a height of approximately 4 μm to the bond interface (d) Sample for SEM observation (e) U-cut is performed (f) Microprobe is attached to the foil by Pt deposition (g) a Mo grid (h) Foil is attached to the Mo grid by Pt deposition.

3.4.7 TEM

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. TEM was used to study the wire bonds morphology and IMC phases at the Cu-Al bond interface in the as-bonded state. This is because the IMC after post bonding is too thin and not possible to observe through the SEM [15]. The beam of electrons from the electron gun is focused into a thin coherent beam by the condenser lens. The beam is restricted by the condenser aperture, which excludes high angle electrons. The beam then strikes the specimen and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion is focused by the objective lens into an image on phosphor screen or charge coupled device (CCD) camera. TEM analysis was performed at 200 kV using a FEI Titan 80-300 TEM. A microprobe beam was used for EDX elemental analysis in scanning transmission STEM mode.

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Chapter 4

Effect of Key Process Parameters on Pd Distribution in Pd-Cu Bonds

Copper (Cu) wire bonding has become a mainstream IC assembly solution due to its significant cost savings over gold wire. However, concerns on corrosion susceptibility and package reliability have driven the industry to develop alternative materials. In recent years, palladium-coated copper (Pd-Cu) wire has become widely used as it is believed to improve reliability. In this chapter, 0.6 mil Pd-Cu and bare Cu wires were studied. The effect of key process parameters on the palladium distribution and grain structure of the Pd-Cu Free Air Ball (FAB) were investigated. It was observed that Electronic Flame Off (EFO) current has a significant effect on palladium distribution in the FAB. The FAB hardness was measured and correlated to palladium distribution and grain structure. First bond process responses were characterized. The impact of palladium on wire bondability and wire bond intermetallic using a high temperature storage test was studied.

4.1 Introduction

Gold wire has been the popular choice of bonding wire for many years. With the continuous increase in the price of gold, mounting pressure was felt by the electronics industry to look for lower cost alternative bonding wires. Copper wire has been rapidly adopted in high volume wire bonding production due to the cost savings over gold wire [1]. In addition, it has better electrical and thermal conductivity compared to gold wire [2]. However, studies have shown that it is susceptible to corrosion under humidity and electrically biased conditions and package reliability is a concern [3]. Another concern with copper wire is its hardness compared to gold which causes pad cratering after bonding in some devices with fragile bond pads [4]. In recent years, palladium-coated copper (Pd-Cu) wire has seen rapid entry into the market and is widely adopted for fine pitch applications. It has a longer shelf life than bare copper wire due to the noble metal coating and is believed to have enhanced bond reliability under humid and electrically biased conditions [5].

As electronic components continue to shrink and advanced devices require high pin counts, 0.6 mil fine palladium-coated copper wire is actively being qualified before being introduced into manufacturing production lines to accommodate such technological developments [6]. Assembly and packaging companies worldwide are known to use different wires from different manufacturers of their choice. Therefore, there is a need to determine optimized Free Air Ball (FAB) and bonded ball parameters for each wire type to maximize the wire bonding capabilities. In addition, with the recent advancements in copper wire technology, the cost factor, and the implication of a Pd coating to the process response, there is a resurgence of interest from customers to run bare Cu despite the advent of Pd-Cu wire. Currently, most wire manufacturers are still debating how Electronic Flame Off (EFO) conditions affect the Pd distribution in the FAB and bonded ball. The effect of Pd distribution on wire bondability and package reliability has not been well understood. In this chapter, ultra-fine pitch processes using 0.6 mil Pd-Cu and bare Cu wires were investigated with the aim to determine optimized process parameters on a K&S IConn ProCu^{PS} ball bonder through a series of systematic FAB and bonded ball experiments. By varying EFO parameters, observation was made on FAB

repeatability and ball shape variation. Next, typical first bond responses for Pd-Cu, in the form of measuring ball size, ball height, ball shear, aluminum pad splash, and wire pull were compared with bare copper wire. All of these bonding experiments were correlated with advanced material analysis to understand the bonding responses from a materials perspective. Palladium distribution and grain structure of the cross-sectioned FABs were studied and analyzed. These were correlated to the bonded ball hardness using an on-bonder hardness measurement technique. Intermetallic formation and growth under unmolded High Temperature Storage (HTS) were also analyzed. The different wire properties, bonding responses, and material analysis results are presented at the end with conclusions on their correlations and implications on device performance.

4.2 Experimental Methods

4.2.1 Preparation of Cu and Pd-Cu Free Air Balls and Bonded Balls

In this study, all FAB and bonded ball testing was performed on a Kulicke and Soffa (K&S) IConn ProCu^{PS} automatic ball bonder using 0.6 mil Pd-Cu and bare Cu wires. A K&S Cupra3G capillary was used for bonding, with a hole diameter of 18 μm , a chamfer diameter of 22 μm and a tip diameter of 50 μm . The wire bonding was run using two types of cover gas (forming gas and nitrogen) for Pd-Cu wire and only forming gas for bare Cu wire. The forming gas is a gas mixture consisting of 95% nitrogen and 5% hydrogen. The flow rate of forming gas or nitrogen was set to 0.5L/min. The FAB in this study was prepared using the “Formed FAB” process on the wire bonder and the FAB diameter was verified using a Nikon Nexiv microscope to ensure a ball size ratio (BSR) of 1.6 and a FAB diameter of 24 μm . Ball size ratio is defined as the FAB diameter divided by the wire diameter.

Thermosonic ball bonding was performed on silicon die with aluminum pads with thickness of approximately 1 μm die-attached on a BGA substrate, using an optimized set of process parameters involving contact velocity (CV), ultrasonic current (USG) and bond force to ensure a bonded ball size of 27 μm and ball height of 7 μm . Process responses such as ball diameter, ball height, ball shear, first bond pull and aluminum pad splash in the USG vibration direction were measured.

4.2.2 Electron Backscattered Diffraction Analysis

Selected FAB samples were cross-sectioned using a FEI Dual-Beam Focused Ion Beam (FIB) system and the grain structure was analyzed using an EDAX Digiview IV Electron Backscattered Diffraction (EBSD) detector. EDAX Orientation Imaging Microscopy (OIM) analysis software was used for grain size and grain orientation analysis.

4.2.3 EDX Analysis

Pd distribution found within the FAB and bonded ball was analyzed using a JEOL JSM-6610 LV Scanning Electron Microscope (SEM) equipped with an Oxford Instrument Inca Energy Dispersive X-Ray (EDX) spectroscope. Pd concentration in the FAB bulk was analyzed using JEOL JXA 8530F Field Emission Electron Probe Micro Analyzer Wavelength Dispersive X-ray (EPMA-WDX).

4.3 Results and Discussions

4.3.1 FAB Repeatability for Pd-Cu and Bare Cu Wires

This chapter compares Pd-Cu FABs from two different wire manufacturers. The Pd content for Type 1 and Type 2 wires provided by Manufacturer A was specified to be 2.8 wt. %. The Pd content for Type 1 and Type 2 wires provided by Manufacturer B was specified to be 2.1 wt. % and 1.6 wt. %, respectively. Forming gas was used to form the FABs unless otherwise stated. EFO firing time was adjusted accordingly to ensure the same ball size ratio of 1.6 for each EFO current setting. FAB repeatability, which is defined by the ability to form the targeted ball size, was tested. Figure 4.1 illustrates that FAB repeatability, defined as relative standard deviation or the ratio of standard deviation over the average FAB diameter, generally improves with increasing EFO current, as shown by the decreasing standard deviation at higher EFO currents. The tendency for FAB repeatability to improve with increasing EFO current is a result of more stable plasma at a high EFO current. In addition at higher EFO current, the fire time are short,

so external factors have a reduced influence on the FAB formation process. Conversely, at a lower current and longer fire time, more heat is lost to conduction into the wire causing more variations. Figure 4.1 also shows that FAB repeatability is similar for Pd-Cu and bare Cu wires and the relative standard deviation for all the wire types generally meets the specification of 1 % of the FAB diameter. In these experiments, the Pd coating thickness did not have a strong influence on FAB repeatability. Next, the effect of cover gas type on FAB repeatability was investigated. As shown in Figure 4.1, FABs formed in nitrogen exhibited degraded repeatability compared to forming gas. This could be due to a higher degree of malformed FABs in nitrogen which could be due to the difference in heating power between nitrogen and forming gas or some remaining oxidation on the FAB in the case of nitrogen. We can conclude that FAB repeatability is affected by EFO current and cover gas type.

Figure 4.1 FAB repeatability for Pd-Cu and Cu wires for a range of EFO currents.

4.3.2 Palladium Distribution in the FAB

The effect of Pd on reliability has been an increasingly debated topic and there is a

need to better understand the effect of Pd distribution on package reliability. Manufacturer A Type 2 wire was selected for the remainder of the analysis. Pd-Cu and bare Cu FABs were bonded at three different EFO current settings (low, mid and high) with different cover gas types (forming gas vs. nitrogen). The FABs were then cross-sectioned to reveal the palladium distribution in the FAB. Optical images were taken using bright field imaging techniques and Pd rich regions were analyzed. SEM–EDX elemental mapping was then used to verify the grey regions to be Pd rich regions. The optical and EDX analysis results are shown in Figure 4.2.

Some malformed balls (“apple bites”) were observed for FABs formed at a low EFO current setting in forming gas, as shown in Figure 4.3. The degree of malformation is worse for FABs bonded in nitrogen compared to forming gas. This can account for the higher relative standard deviation in FAB diameter when using nitrogen. The apple bite effect can be explained, at least in part, by the different heating effect of forming gas and nitrogen [7]. For bare Cu wire, no malformed balls were observed at both low and high EFO currents. It is to be noted here that this particular Pd-Cu wire tested is a prototype wire and similar test conditions were repeated with the latest wire provided by the wire supplier, and no malformed balls were observed at the low EFO current in nitrogen.

With forming gas and a low EFO current setting, a thin uniform ring of Pd-rich phase was observed around the FAB periphery, with Pd found at the FAB tip. A higher EFO current produces a steeper temperature gradient, causing Cu to flow out at a faster rate. Hence, at a mid EFO current setting, the Pd-rich phase mostly concentrates at the neck region of the FAB. At an even higher EFO current, the Pd-rich phase is mostly at the periphery neck, with some infusion of Pd into the FAB bulk. This is due to the turbulent flow of Cu and partial melting of Pd, causing random distribution of Pd in the FAB bulk. With nitrogen gas and a mid EFO current setting, a Pd-rich layer was seen around the periphery, with Pd found near the tip. It was observed that Pd and Cu do not form a homogeneous solid solution at all EFO currents settings, resulting in Pd rich areas. The heat energy generated by the EFO spark might not be sufficient to melt the Pd completely as a large component of it is being used to supply the heat of fusion of Cu. The Pd rich regions detected by EDX elemental maps were observed to correlate well with the grey regions in the optical images. From the analysis, it can be concluded that

EFO current has a strong influence on Pd distribution in the FAB.

Figure 4.2 FAB cross-sections for Pd-Cu wires.

Figure 4.3 Example of an apple bite FAB.

4.3.3 Grain Structure along the FAB

Apart from determining palladium distribution in the FAB, the grain structure of the FAB was analyzed. FABs were cross-sectioned along the wire direction using dual-beam FIB and the grain structure was analyzed in situ using an EBSD detector attached to the FIB system. This polishing technique, using a dual-beam FIB, allows a fine surface finish ideal for obtaining diffraction patterns. Sample preparation in situ and under vacuum prevents oxidation of samples which will degrade the observation. From Figures 4.4 and 4.5, it can be seen that grain growth in the FAB region is along the wire direction. This is due to the temperature gradient from the tip of the ball to the wire, produced when the wire tip is melted by the EFO spark. The grain is coarser at the FAB compared to the wire. As the wire is melted, the temperature at the Heat Affected Zone (HAZ) increases which leads to grain recrystallization and grain growth. In gold wire bonding, the grains at the HAZ were observed to be coarser than the virgin wire [8]. However, from Figure 4.4, it was observed that the HAZ region cannot be easily distinguished from the virgin wire. This was also observed for bare copper wire as shown in Figure 4.5. This could be due to the gradual transition in grain size going from the HAZ to the virgin wire. Also, it could be due to annealing as part of the Cu and Pd-Cu wire manufacturing process which results in recrystallized uniaxial grains in the wire.

Figure 4.4 EBSD image of Pd-Cu wire bonded at low EFO current in forming gas.

Figure 4.5 EBSD image of Cu wire bonded at low EFO current in forming gas.

4.3.4 Grain Structure Analysis across the FAB

Since the grain structure across the FAB directly impacts the ball bonding process, a cross-section was performed across the FAB, with grain size and grain orientation data being collected. Figure 4.6 shows the grain structure for the FABs at different EFO currents and cover gas types (forming gas vs. nitrogen). No preferential orientation was observed for all FABs bonded at the different settings except for Pd-Cu FAB bonded at low EFO current in forming gas. The Pd-Cu FAB formed at low EFO current in forming gas appears to have some form of preferred orientation in between the [001] and [111] directions. For polycrystalline Cu, the Young's modulus for the orientations is in the order of $[111] > [101] > [001]$. Since the preferred orientation lies in between the smallest and largest modulus, hence the preferred orientation in the bulk copper material for the low EFO current setting should not have significant influence to the stiffness or bondability of the FAB on the Al bond pad. For Pd-Cu FAB bonded at low EFO current, a continuous ring of small grains was observed at the peripheral of the FAB. For Pd-Cu FAB bonded at mid EFO current, a discontinuous ring of small grains was observed at the peripheral of the FAB. No small grains were observed at the peripheral for bare Cu FAB. These smaller grains at the FAB peripheral could be from the Pd-rich phase. These smaller grains correspond well with the FAB Pd distribution shown in Figure 4.2.

The FAB grain size was calculated by discounting the smaller grains at the FAB periphery. An individual value plot and box plot of the grain size were obtained using

Minitab 15 statistical software as shown in Figures 4.7a and 4.7b. From the individual value plot, it can be seen that there is a large variation in the individual grain size. The mean grain size value was observed to be smaller at a higher EFO current, with the difference in grain size around 0.5 μm as shown in Table 4.1. However, since the data spread is similar as shown in the box plot, the grain size at low and high EFO currents are not considered to be significantly different. Cover gas type has no significant effect on the grain size. There is no significant difference in grain size between Pd-Cu and bare Cu FAB as the FAB bulk is essentially copper for both Pd-Cu and bare Cu wire.

According to the Hall–Petch Equation, the yield strength varies with the grain diameter according to equation 4.1:

$$\sigma^y = \sigma_0 + k_y d^{-\frac{1}{2}} \quad (4.1)$$

where d is the average grain diameter. σ^y and k_y are constants for a particular material.

For copper, $\sigma_0 = 25 \text{ MPa}$ and $k_y = 0.11 \text{ MPa m}^{1/2}$ [10].

A fine grained material is harder and stronger than one that is coarse grained as the former has more grain boundaries to impede dislocation motion. Based on the results, it can be deduced that the FAB hardness is not influenced by the bulk copper as the copper grain size in the FAB is similar across all settings.

Figure 4.6 EBSD image of Pd-Cu and bare Cu wire across the FAB.

Figure 4.7a Individual value plot of FAB grain size at different settings.

Figure 4.7b Box plot of FAB grain size at different settings.

Table 4.1 Mean grain size for Pd-Cu and bare Cu FABs

Wire Type	Gas Type	EFO current	Mean grain size (μm)
Pd-Cu	Forming gas	Low	5.28
		Mid	4.65
	Nitrogen	Low	5.05
		Mid	4.56
Bare Cu	Forming gas	Low	5.26
		Mid	4.48

4.3.5 Palladium Composition in the FAB Bulk

EPMA-WDX point analysis was used to analyze and verify the Pd concentrations inside the FAB bulk as it provides a quantitative chemical analysis and is able to detect a trace concentration of Pd. The analysis was done on Pd-Cu FABs formed at low and mid-level EFO currents, in forming gas and nitrogen. Figure 4.8 shows an EPMA image with point analysis done in the FAB bulk. The concentration of Pd in the FAB bulk is out of the detection limit of 0.036 wt.% Pd. We can conclude that most of the Pd stays at the FAB periphery and does not diffuse into the FAB bulk.

Figure 4.8 EPMA image of point analysis on Pd-Cu FAB

4.3.6 FAB Hardness

As the hardness of a FAB affects its bondability on an aluminum pad [8], a hardness test was performed on the FABs. FABs were bonded onto a test chip using the same first bond parameters and the FAB hardness was measured using an in situ hardness measurement technique on the wire bonder. This technique gives an overall FAB hardness sensitive to the FAB tip compared to a nano-indentation test which gives a more localized hardness measurement. A sample size of 10 wires was taken. FAB hardness can be affected by a few factors as illustrated by the impact diagram in Figure 4.9. FAB hardness index number, defined as the relative squash of the FAB under an applied bonding force for different EFO current settings and gas types is shown in Table 4.2. As expected, the hardness value of Pd-Cu FABs is higher than that for bare copper FABs due to the presence of Pd which is harder than Cu. For bare Cu, the FAB hardness does not appear to be dependent on EFO current. However for Pd-Cu wire, it was also observed that FAB hardness is strongly influenced by the EFO current. A low EFO current produced a slightly harder Pd-Cu FAB compared to a high EFO current. As discussed earlier, lower EFO current results in a thin Pd presence at the FAB tip while a higher EFO current results in Pd concentrated at the FAB neck. The presence of Pd at the FAB tip could have resulted in the increased overall hardness of the FAB. The hardness at the low EFO current setting was about 7 % higher compared to the mid EFO current which may not be significantly different depending on pad sensitivity.

Figure 4.9 Impact diagram showing factors affecting FAB hardness.

Table 4.2 Hardness index for Pd-Cu and bare Cu FABs.

Wire Type	Gas Type	EFO current	Hardness index	Stdev
Pd-Cu	Forming gas	Low	18.42	0.543
		Mid	17.22	0.642
		High	18.30	0.944
	Nitrogen	Low	18.36	0.849
		Mid	17.31	0.783
		High	18.12	1.021
Bare Cu	Forming gas	Low	16.30	0.548
		Mid	16.10	0.784

4.3.7 First Bond Process

The presence of Pd at the FAB tip might form a Pd-rich layer at the bond interface affecting wire bond reliability. First bond parameters were optimized to produce the desired shear strength. EFO firing time was adjusted across the different EFO settings to obtain a bonded ball diameter of 27 μm and a bonded ball height of 7 μm . The same first bond parameters were then applied for all of the EFO current settings. All first bond work was performed in forming gas.

Figure 4.10 shows the Pd distribution of the bonded balls. It was observed that the low EFO current setting does not produce a visible Pd-rich layer at the interface. This might be due to the thin Pd-rich layer at the FAB periphery. A visible layer of Pd-rich region was found at the bond interface with the optimized low EFO current setting. For the mid EFO current setting, the presence of Pd was found at the bond interface. For the high EFO current setting, some Pd infusion was observed in the bonded ball. It was observed that there is no systematic trend like the case of the FAB and also there is a slight variation in the concentration of Pd at the bond interface within the same setting. This could be due to the Pd coating thickness variation in the Pd-Cu wire or an USG effect.

There is no significant difference in the first bond process response for the different EFO current settings as shown in Table 4.3. The process window is defined as the range of a bonding parameter (typically USG current) that does not show lifts or peels in a pull test [11]. From Figure 4.11, it can be seen that the process window is similar for mid and high EFO current settings. The optimized low EFO current improved the process window giving less ball lifts and pad peels and a bigger window which is probably because this setting gives the best FAB size consistency. It can be seen that FAB hardness and the presence of Pd at the tip does not have a significant effect on the wire bondability. The presence of Pd at the bond interface did not result in more pad peels. This can be attributed to the insignificant difference in FAB hardness between the low and high EFO currents as shown in Table 4.2.

Figure 4.10 EDX elemental map showing Pd distribution for bonded ball at various EFO current settings.

Table 4.3 First bond process response for Pd-Cu wire

Process Response	Optimized Low EFO current	Mid EFO Current	High EFO Current
Ball Diameter (μm)	27.63	27.60	27.90
Ball Height (μm)	7.59	7.33	7.43
Aluminum Splash (μm)	32.27	32.11	32.51
Shear (g)	8.54	8.21	8.71
Shear/Area (g/mil^2)	9.2	8.9	9.2
Pull Average (g)	5.59	5.43	5.73
Pull Min (g)	5.10	5.02	5.14

Figure 4.11 Process windows for different EFO current setting in forming gas.

4.3.8 High Temperature Storage

It is of interest to study how the Cu–Al interfacial reaction and morphology are affected by the presence of Pd at the bond interface. Unmolded bonded samples for the optimized low EFO current setting bonded in forming gas were subjected to High Temperature Storage (HTS) at 175 °C in an air environment for up to 168 h.

Cross-sections of the bonded ball at different annealing durations were analyzed. It was reported that nano voids were present at the bond interface of Pd-Cu bonds in the as-

bonded state [12]. As shown in Figure 4.12, numerous nano voids were observed in the as-bonded state along the bond interface and at the ball neck periphery. These are the areas where there is a presence of Pd and it can be seen that nano voids are strongly related to the presence of Pd. The presence of voids in the as-bonded state suggests that they could have been formed during the formation of FABs and the exact cause remains unclear. A possible explanation could be due to the difference in diffusivity of Cu and Pd in each other, and unbalanced inter-diffusion may cause the formation of the voids. Voids are present at the bond central and bond periphery in the as-bonded state and after annealing as shown in Figure 4.13.

Figure 4.14 shows the IMC growth with annealing time. The growth rate of Cu–Al IMC is slow and exhibits an island type of morphology as shown in Figure 4.14 after annealing for 168 h. There is no visible IMC at the interface in the as-bonded state as shown in Figure 4.14b. This is due to the resolution limit of SEM and a more accurate analysis can be provided by Transmission Electron Microscope (TEM). Xu et al. [13] reported that ~20 nm island-like CuAl_2 IMC particles have been formed in the as-bonded state. Two layers of IMCs were formed at 24 h and 168 h annealing time, one close to the Cu bond and the other abutting the Al pad. Singh et al. [11] also reported two layers of IMCs, namely CuAl_2 and Cu_9Al_4 after 24 h and 168 h of annealing. The two layers of IMCs were observed to be separated in some regions at 24 h and the gap increased at 168 h. The native aluminum oxide layer could be broken down during IMC formation, forming a discontinuous layer between the IMCs.

Tests were done to determine the first bond pull value and process window after annealing at 24 h and 168 h. The results for pull strength are given in Table 4.4 and the process window at different annealing durations is shown in Figure 4.15. Although the process window shrinks drastically with annealing time with no process window found at 168 h, the pull values only decreased slightly. The increase in pad peels with annealing time can be attributed to the growth of IMC both laterally and vertically which resulted in an irregular volume increase over that of the original Al metallization. The resultant stress could contribute to more pad peels over time.

Figure 4.12 Nano voids formed in the Pd-Cu wire bond in the as-bonded state

Figure 4.13 Voids in (a) left periphery, (b) centre, and (c) right periphery of bond interface at different annealing time.

Figure 4.14 Comparison of IMC growth along (a) entire bond interface with yellow box showing the zoomed in sections and at (b) zoomed in sections.

Table 4.4 First bond pull value for Pd-Cu bonds at optimized low EFO current setting.

Process Response	0 h	24 h	168 h
Pull Average (g)	5.59	5.44	4.88
Pull Min (g)	5.10	5.03	4.27
Stdev	0.2	0.4	0.46

Process Window for Optimized Low EFO Current Setting at Different Aging Duration

Figure 4.15 Process windows for optimized low EFO current setting at different annealing

durations.

4.4 Conclusions

Pd-Cu wire has recently been widely adopted for bonding of fine pitch devices due to its longer shelf life, stitch bond robustness and enhanced reliability. This work investigates the effect of key process parameters on the palladium distribution and grain structure in Pd-Cu FAB. The following conclusions can be made based on the investigations.

1. Pd distribution was shown to be strongly influenced by the EFO current and cover gas type, with the EFO current being the main factor. At low EFO current, the Pd rich phase is concentrated at the bond interface. At high EFO current, there is turbulent flow of Cu and partial melting of Pd, causing random distribution of Pd in the FAB bulk.
2. EFO current and cover gas type has no significant effect on the grain structure such as grain size and grain orientation of Pd-Cu and Cu FABs.
3. The hardness of the FABs was measured using an on-bonder squash measurement. Hardness value of Pd-Cu FABs was observed to be higher than that for bare copper FABs due to the presence of Pd which is harder than Cu. For bare Cu wire, the FAB hardness does not appear to be dependent on EFO current. However for Pd-Cu wire, FAB hardness is strongly influenced by the EFO current. A low EFO current produces a slightly harder Pd-Cu FAB compared to a mid EFO current due to the presence of Pd at the FAB tip.
4. Nano voids were observed in the as-bonded Pd-Cu bonds and were found to be strongly related to the presence of Pd. Two layers of IMCs were observed after annealing the Pd-Cu bond at 175°C for 24 and 168 h.

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Chapter 5

Effect of Palladium on the Mechanical Properties of Cu-Al IMCs

There is growing interest in copper (Cu) wire bonding due to its significant cost savings over gold wire. Recently, palladium coated copper (Pd-Cu) wire has been widely used in fine pitch applications as it is believed to improve reliability of copper wire bonds on aluminum (Al) pads. However, the effect of palladium on the mechanical properties and corrosion resistance of Cu and Cu-Al intermetallic compounds (IMCs) has not been studied in detail. In this chapter, bulk alloys of Cu and Cu-Al intermetallic compounds with different concentrations of Pd were studied. Among the three IMCs studied, CuAl ($H \sim 8.5$ GPa) was found much harder than CuAl₂ and Cu₉Al₄ ($H \sim 6.0$ GPa). Young's moduli of CuAl and Cu₉Al₄ IMCs were around 155 GPa and are much stiffer than the one for CuAl₂ (~ 110 GPa). The addition of a few percent Pd only slightly increases the hardness and Young's modulus of the IMCs.

5.1 Introduction

In Chapter 4, it was observed that the palladium distribution in Pd-Cu wire bonds can be varied by adjusting the EFO current. Two conditions of palladium distributions were obtained, with and without the presence of palladium at the bond interface. The presence of palladium at the bond interface can affect the mechanical properties of Cu wire bonds and the Cu-Al intermetallic compounds. This would subsequently have an effect on the amount of pad peels and cratering in the as-bonded state and after thermal annealing. In this chapter, the mechanical properties such as the modulus and hardness of pure Cu and Cu-Al IMCs with addition of Pd were investigated.

Two kinds of intermetallic compounds, CuAl_2 and CuAl were formed in friction welded Al/ Cu interface after annealing at 773 K for 129.6 ks [1]. Cu and Al were mechanically alloyed during ball milling of Cu and Al powders. With thermal annealing of the as-milled composite powders, CuAl_2 were formed first followed by Cu_9Al_4 [2]. In a recent study on ultra-fine (15 μm) Pd-Cu wire bonds on Al bond pads [3], Pd was detected on the free air ball surface, which will affect the composition of the wire bond and IMC at the bond interface. Electronic flame off current and the type of cover gas used, were found to influence the Pd distribution [3]. So far, information on the impact of the addition of palladium on the mechanical properties of pure Cu and Cu-Al IMCs has not been available.

In this chapter, the mechanical properties of three types of Cu-Al IMCs, namely CuAl_2 , CuAl and Cu_9Al_4 , that can be present between the bonded ball and aluminum pad during the ball bonding process and after thermal annealing, are reported. Effects of the addition of palladium on the properties of Cu and Cu-Al IMCs will be investigated. Cu and Cu-Al IMCs with different Pd concentrations (up to 10 wt.% replacement of Cu in the alloy) were prepared using an arc melter in an argon gas environment. The samples were then mounted and cross-sectioned to check the sample homogeneity. Scanning Electron Microscope-Energy Dispersive X-ray spectroscopy (SEM-EDX) and X-ray diffraction (XRD) were employed to investigate the elemental composition and phase formation of Cu-Al IMCs. Nanoindentation tests were performed to measure the elastic modulus and hardness. The results provide fundamental information on the effect of Pd

alloying on the phase formation and mechanical properties of Cu and Cu-Al IMCs, which will be useful for Pd-Cu wire bonding and reliability.

5.2 Experimental Methods

5.2.1 Materials

Elemental Cu, Al and Pd with 99.95% purity were commercially obtained from Sigma–Aldrich. The metal alloys were prepared by arc melting elemental Cu, Al and Pd under an argon atmosphere to prevent oxidation during melting. The metal alloys were re-melted several times for better composition homogeneity. The total weight of each alloy sample is approximately 1 g. The alloys were then mounted and cross sectioned using Si–C papers till grit #2400 and polished with diamond paste progressively until 1 μm size.

5.2.2 Microstructures

Material composition of the metal alloys was analyzed using a JEOL JSM-6610LV Scanning Electron Microscope (SEM) equipped with an Oxford Instrument Inca Energy Dispersive X-ray (EDX) analyzer. An accelerating voltage of 15 kV was used for the EDX analysis. Structural characterization was performed using a Shimadzu 6000 X-ray diffractometer (XRD) and Cu $K\alpha$ radiation (wavelength 1.5418 Å) at 40 kV and 30 mA. Phase quantification was carried out by Rietveld refinement using the software Topas Academic v.4.1. In Rietveld refinement, the intensity profile is fitted to structural model using a least square calculation. The calculated intensity is based on the crystallographic structures and XRD instrumental parameters. The background was fitted using a 7th order Chebyshev polynomial function.

5.2.3 Nanoindentation

The indentation tests were performed with a MTS Nanoindenter XP[®] system using a Continuous Stiffness Measurement (CSM) technique [4]. Using this technique, during

loading, a small oscillatory force with a frequency of 45 Hz and amplitude of 2 nm was imposed on the nominal load to extract contact stiffness (S) as a continuous function of the indenter's displacement into the sample. The tests were performed using Berkovich tip. The Berkovich tip is a three-faced pyramid with a radius around 50 nm at the apex. The indenter was pressed into the materials at a constant strain rate of 0.05 s^{-1} . The maximum depth approached into all samples was 2000 nm. Ten indentation points at different locations were made for each of the samples. The reported modulus and hardness were extracted from the loading process as the average values in the depth range from 1600 to 1800 nm. At this depth range, the modulus and hardness values were stabilized. The hardness and stiffness are calculated using the equations described in Section 3.4.4.

5.3 Results and Discussions

5.3.1 EDX and Compositional Analysis

In Cu and Cu–Al IMCs with different Pd concentrations (0, 1, 3 and 10 wt.% replacement of Cu) were prepared by arc melting the metals in an argon gas environment to minimize oxidation. The sample was named after the intended crystalline compound. The obtained crystal structure will be discussed later based on the XRD results. The samples were cross-sectioned and an EDX point analysis was performed. Six points were used to check for sample homogeneity (Figure A.1, Appendix). The EDX analysis results are shown in Tables 5.1a to 5.1d. The detailed EDX results at different points in the sample are shown in Tables A.1 to A.4 in Appendix. The alloy samples exhibit quite good homogeneity based on SEM observation, except that the Pd distribution in the Al-rich samples was not as uniform as the Cu-rich samples. Some Pd segregation was also observed at high Pd concentrations at 10 wt.% Pd as shown in Figure A.2 in Appendix.

Table 5.1a EDX composition analysis of Cu alloys (wt. %).

Sample	Element	Average	Ideal	Stdev	Crystal Structure
Pure Cu	Cu	100.0	100.0	0.0	Face-centered cubic
Cu-1%Pd	Cu	98.8	99.0	0.0	Face-centered cubic
	Pd	1.2	1.0	0.1	
Cu-3%Pd	Cu	96.9	97.0	0.1	Face-centered cubic
	Pd	3.1	3.0	0.1	
Cu-10%Pd	Cu	90.1	90.0	0.0	Face centered cubic
	Pd	9.9	10.0	0.0	

Table 5.1b EDX composition analysis of Cu₉Al₄ alloys (wt. %).

Sample	Element	Average	Ideal	Stdev	Crystal Structure
Cu ₉ Al ₄	Cu	85.6	84.1	0.1	Primitive cubic
	Al	14.5	15.9	0.1	
(Cu-1%Pd) ₉ Al ₄	Cu	85.3	83.3	0.1	Primitive cubic
	Al	13.9	15.9	0.1	
	Pd	0.80	0.84	0.0	
(Cu-3%Pd) ₉ Al ₄	Cu	82.9	81.6	0.1	Primitive cubic
	Al	14.1	15.9	0.1	
	Pd	3.0	2.5	0.1	
(Cu-10%Pd) ₉ Al ₄	Cu	77.0	75.7	0.1	Primitive cubic
	Al	14.3	15.9	0.1	
	Pd	8.6	8.4	0.0	

Table 5.1c EDX composition analysis of CuAl alloys (wt. %).

Sample	Element	Average	Ideal	Stdev	Crystal Structure
CuAl	Cu	71.0	70.2	0.5	Side-centered monoclinic
	Al	29.1	29.8	0.5	
(Cu-1%Pd)Al	Cu	71.3	69.5	1.3	Side-centered monoclinic
	Al	27.2	29.8	1.8	
	Pd	1.5	0.7	0.6	
(Cu-3%Pd)Al	Cu	69.6	68.1	1.0	Side-centered monoclinic
	Al	27.6	29.8	1.6	
	Pd	2.8	2.1	0.5	

(Cu-10%Pd)Al	Cu	66.4	63.2	2.3	Side-centered monoclinic
	Al	27.6	29.8	1.6	
	Pd	6.0	7.0	0.7	

Table 5.1d EDX composition analysis of CuAl₂ alloys (wt. %).

Sample	Element	Average	Ideal	Stdev	Crystal Structure
CuAl ₂	Cu	56.2	54.1	1.5	Body-centered tetragonal
	Al	43.8	45.9	1.5	
(Cu-1%Pd)Al ₂	Cu	53.5	53.5	0.0	Body-centered tetragonal
	Al	45.3	45.9	0.4	
	Pd	1.2	0.5	0.5	
(Cu-3%Pd)Al ₂	Cu	54.5	52.5	1.4	Body-centered tetragonal
	Al	44.2	45.9	1.2	
	Pd	1.3	1.6	0.2	
(Cu-10%Pd)Al ₂	Cu	51.8	48.7	2.2	Body-centered tetragonal with some Cu ₃ Al ₂ (rhombohedral) and Al (f.c.c)
	Al	43.9	45.9	1.4	
	Pd	4.3	5.4	0.8	

5.3.2 XRD Analysis

XRD analysis was performed to ensure that the correct IMC phases were formed. The scanning angle ranges from $2\theta = 10^\circ$ to 100° . The XRD spectra for the samples are presented in Figures 5.1 to 5.4. The desired IMC phase was indeed present (Tables 5.1a to 5.1d) in all the samples except for the (Cu-10%Pd)Al₂ where other phases were detected. More detailed analysis for this sample will be provided later.

As shown in Figure 5.1a for Cu-Pd alloys, the peaks at $2\theta = 43.3^\circ$, 50.5° , 74.2° and 90.0° correspond well to the (111), (200), (220) and (311) planes of face-centered cubic (f.c.c.) Cu (ICDD entry #00-004-0836). From Figure 5.1b, peak shift was observed with the addition of Pd. According to Bragg's Law, the incident ray angle is related to the atomic plane spacing according to the equation described in Section 3.4.3. Increasing the Pd content leads to increased lattice constant and lattice volume due to the larger atomic radius of Pd compared to Cu. This leads to a peak shift towards lower diffraction angles

according to Bragg's Law.

As shown in Figure 5.2, the characteristic peak at $2\theta = 44.2^\circ$ corresponds well to the (330) plane of primitive cubic Cu_9Al_4 (ICDD entry #00-024-0003). The peaks in Figure 5.3 at $2\theta = 43.8^\circ$, 44.2° , 44.7° , and 45.1° correspond well to the (-512), (020), (-511) and (-313) planes of side-centered monoclinic CuAl (ICDD entry #00-026-0016). From Figure 5.4, the peaks at $2\theta = 36.9^\circ$, 38.0° , 42.2° , 42.7° , 47.4° and 47.9° correspond well to the (002), (211), (220), (112), (310) and (202) planes of body-centered tetragonal CuAl_2 (ICDD entry #04-013-4023). However, for the intended (Cu-10%Pd) Al_2 sample, other phases were formed. This could be due to the increased concentration of Pd causing reduced homogeneity of the sample. For all the samples, no Pd peaks are detected, which is an indication that most of the Pd is present within the desired phases.

Rietveld refinement was carried out for the (Cu-10%Pd) Al_2 sample to quantify the phases present. Good agreement was obtained between experimental and calculated diffraction intensities. The results revealed that the sample contained 59.6% of CuAl_2 , 31.1% of Cu_3Al_2 and 9.3% of Al (Figure 5.5). The R-factor obtained for the sample was $R_{wp} = 5.66$. The R-factors obtained for the phases were: $R_{BRAGG_CuAl_2} = 5.665$; $R_{BRAGG_Cu_3Al_2} = 1.287$ and $R_{BRAGG_Al} = 2.998$.

Figure 5.1a XRD patterns of Cu-Pd alloy samples.

Figure 5.1b XRD peaks shift with Pd addition.

Figure 5.2 XRD patterns of Cu_9Al_4 alloy samples.

Figure 5.3 XRD patterns of CuAl alloy samples.

Figure 5.4 XRD patterns of CuAl_2 alloy samples.

Figure 5.5 Rietveld analysis of $(\text{Cu-10\%Pd})\text{Al}_2$ sample.

5.3.3 Nanoindentation Results

Figure 5.6 shows typical load vs indentation depth curves of the Cu and Cu–Al IMCs samples. Figures 5.7 and 5.8 show the elastic modulus (E) and hardness (H) of samples tested at a strain rate of 0.05 s^{-1} . The detailed values with standard deviation are

listed in Table 5.2. The pure Cu sample has a much lower hardness than the Cu–Al IMC samples. Overall, the elastic modulus of the alloys increases slightly by addition of Pd. The enhancement of elastic modulus of the Cu–Al–3 wt.% Pd IMCs is due to the Pd solute in the lattice. With further increase in Pd concentration, the modulus of the samples is slightly reduced (e.g. at 10 wt.% replacement). This might be due to segregation of Pd as the lattice may not be able to accommodate the large strain caused by Pd replacement at the Cu lattice location (Figure A.2 in Appendix).

In general, the addition of Pd slightly increases sample hardness at smaller concentrations. This is due to solid-solution hardening, as the Pd solute imposes lattice strains on the surrounding atoms. This strain field interacts with dislocations, and consequently, dislocation motion is restricted. This leads to increasing strength and hardness. However, increasing the concentration of Pd from 3 to 10 wt.% seems to decrease alloy hardness. This could be due to a similar reason as that provided for the decrease in elastic modulus. Among all IMC samples evaluated, CuAl IMC exhibited the highest hardness and modulus while CuAl₂ IMC possesses the lowest modulus and hardness. The results are consistent with an earlier report where CuAl was revealed to be more brittle and harder compared to CuAl₂ based on density function theory [5]. Overall Pd addition increases the hardness and modulus of the samples slightly up to 3 wt.% replacement.

Pad cracking is a known bonding problem closely related to the bonding force used. Copper wire bonding requires higher bond force than gold wires because of its higher hardness. In the current work, it was found that Pd addition does not lead to a large increase in the Cu wire hardness. This implies that the bond force required for Pd–Cu wire bonding will not be significantly higher than that for pure Cu wire. Qin et al. reported that bare Cu and Pd-Cu wires can be bonded with similar first bond parameters [8].

Xu et al. reported that CuAl₂ forms first during bonding. After annealing at 175 °C for 25 h, an IMC bilayer forms with CuAl₂ close to the Al pad and Cu₉Al₄ abutting the Cu bond [6]. In another report, CuAl was observed to be formed in between Cu bond and CuAl₂ after annealing at 175 °C for 1000 h [7]. The Cu–Al IMC thickness was reported to be lower for Pd–Cu wire bonds compared to bare copper wire bonds. Pd was observed

to reduce IMC growth in the Pd–Cu wire bonds [8]. Pad peel occurs when the bond strength at the bond interface is lower than the wire strength. Peeling rate for wire pull tests could be expected to increase drastically after thermal annealing. This is due to volumetric stresses induced on the pads by the growth of Cu–Al IMCs. Also from the results, Cu–Al IMCs generally has a higher stiffness (especially after long-term annealing) than Cu, resulting in stress build up in the pads. Since the addition of Pd increases Young's modulus of Cu–Al IMC slightly, Pd–Cu wire bonds will be expected to have a slightly higher peeling rate compared to bare Cu wire bonds. More research is needed to assess the impact on long-term reliability of Pd–Cu wire bonding.

Figure 5.6 Load displacement curves of Cu and Cu-Al IMCs at strain rate of 0.05s^{-1} .

Figure 5.7 Elastic modulus of pure Cu and Cu-Al alloys with different Pd concentrations. The modulus was measured at strain rate of 0.05s^{-1} .

Figure 5.8 Hardness of pure Cu and Cu-Al alloys with different Pd concentrations. The modulus was measured at strain rate of 0.05s^{-1} .

Table 5.2 Modulus and hardness of pure Cu and Cu-Al samples at different Pd wt.%.

Samples	Modulus (GPa)	Hardness (MPa)
Pure Cu	110.1 ± 1.69	0.84 ± 0.01
Cu-1%Pd	106.6 ± 1.36	0.79 ± 0.02
Cu-3%Pd	114.8 ± 2.45	0.93 ± 0.00
Cu-10%Pd	119.4 ± 2.03	0.91 ± 0.01
CuAl ₂	112.0 ± 1.14	6.00 ± 0.05
(Cu-1%Pd)Al ₂	108.5 ± 6.42	6.46 ± 0.10
(Cu-3%Pd)Al ₂	116.5 ± 3.17	5.97 ± 0.21
(Cu-10%Pd)Al ₂	107.8 ± 1.26	5.59 ± 0.31
CuAl	155.1 ± 4.25	8.51 ± 0.33
(Cu-1%Pd)Al	154.9 ± 3.71	8.63 ± 0.15
(Cu-3%Pd)Al	169.1 ± 1.29	8.81 ± 0.07
(Cu-10%Pd)Al	144.5 ± 1.64	7.58 ± 0.12
Cu ₉ Al ₄	153.2 ± 1.63	6.11 ± 0.05
(Cu-1%Pd) ₉ Al ₄	161.4 ± 0.59	6.39 ± 0.13
(Cu-3%Pd) ₉ Al ₄	169.9 ± 2.04	6.45 ± 0.09
(Cu-10%Pd) ₉ Al ₄	136.9 ± 1.80	5.79 ± 0.05

5.4 Conclusions

A systematic study on palladium's effect on phase formation and mechanical properties of pure Cu and Cu–Al IMCs (Cu₉Al₄, CuAl, CuAl₂) was carried out. The SEM–EDX analysis results generally showed good composition homogeneity. The XRD results confirmed the formation of the desired IMC phases. The XRD diffraction peaks shifted towards lower diffraction angles as the Pd concentration increased, which means increase of the lattice parameters with increasing Pd. The nanoindentation results gave a comparison of mechanical properties between Cu and Cu–Al IMCs for different palladium concentration. The following conclusions can be made based on the investigations:

1. The addition of Pd slightly increases the hardness and stiffness of Cu and Cu-Al IMCs. The modulus and hardness of the samples slightly increased for up to 3 wt. % Cu replacement by Pd. However, increasing the concentration of Pd from 3 to 10 wt.%

- seems to decrease alloy hardness which might be due to some inhomogeneity in the samples
2. Pd addition does not lead to a large increase in Cu hardness. This further implies that the bond force required for Pd-Cu wire bonding will not be significantly higher than bare Cu.
 3. Cu-Al IMCs were observed to have a higher stiffness and hardness than pure Cu.
 4. Among the three types of IMCs investigated, CuAl exhibits the highest hardness, while CuAl and Cu₉Al₄ the highest stiffness among the investigated Cu–Al IMCs.

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Chapter 6

Evaluation of the Corrosion Performance of Cu-Al IMCs with Pd Addition

Bare Cu wire bonds were reported to fail molded humidity reliability tests, with Cu_9Al_4 IMC layer being corroded. However, the corrosion susceptibility of the individual Cu-Al IMCs has not been investigated. In addition, the effect of palladium addition on the corrosion resistance of Cu and Cu-Al IMCs has not been reported. This chapter compares the electrical impedance and corrosion performance of the three types of Cu-Al IMCs in an acidic chloride medium by employing electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The analysis of the potentiodynamic polarization results was performed using Tafel extrapolation. A comparison was made with pure Cu and Al. The effect of Pd addition on the IMC corrosion performance has also been studied. Among the three Cu-Al IMCs, Cu_9Al_4 was observed to have the largest corrosion rate followed by CuAl_2 and CuAl . For the metals, Cu was observed to have the lowest corrosion rate and Al is the most easily corroded. The addition of Pd of up to 10 wt. % replacement of the Cu in the alloys slightly improves the corrosion resistance of the metals and IMCs.

6.1 Introduction

As highlighted in literature review, bare Cu wire bonds have poor corrosion performance in molded humidity reliability test due to the interaction of moisture with chlorine in epoxy mold compounds that attack copper in the first bond. However, the effect of Pd on the corrosion resistance of Pd-Cu wire bonds in humidity reliability tests has been ambiguous and it was not ascertained if Pd improves the reliability of the wire bonds. In Chapter 4, it was shown that Pd can be present at the bond interface after free air ball formation with adjustment of the process parameters. The concentration of Pd at the wire bond interface can have an effect on the reliability of the wire bonds in humid conditions. In addition with thermal annealing, Pd could diffuse into the IMC layers, affecting the corrosion resistance of the IMCs and long term reliability of packaged devices.

In this chapter, the corrosion performance is studied for Cu, Al and three types of Cu-Al IMCs (CuAl_2 , CuAl and Cu_9Al_4) in an acidic chlorine solution simulating the conditions in epoxy molded packages [1, 2]. In addition, the effect of the addition of palladium on the corrosion resistance of the samples will be evaluated. Cu, Al and Cu-Al IMCs with different Pd concentrations (up to 10% weight replacement of Cu in the alloy) were prepared in an earlier study using an arc melter in an argon gas environment. The samples were then mounted and cross-sectioned to check the sample homogeneity. Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) and X-Ray diffraction (XRD) were employed to investigate the elemental composition and phase formation of Cu-Al IMCs [3]. Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization were employed to study the corrosion performance of the samples in the electrolyte. The electrochemical test of the individual metals and alloys in the acidic chloride medium were performed to provide a pure environment for the corrosion test, eliminating effects from other factors such as the bonding wire quality, wire bonding parameters, Al pad profile, the consistency of the properties of the epoxy mold compound etc. which might affect the corrosion rate. The results provide fundamental information on the corrosion susceptibility of Cu, Al and Cu-Al IMCs which will be useful for Pd-Cu wire bonding and reliability.

6.2 Experimental Methods

6.2.1 Materials and Microstructures

Cu and Cu-Al IMCs with varying concentrations of palladium addition were prepared and phase composition verified based on the work reported in Chapter 5.

6.2.2 Electrochemical Tests

Prior to the electrochemical experiments, each metal sample was grinded and polished to remove the oxidation film, degreased with ethanol ultrasonically for 3 minutes, washed with deionized water and blown dry. The polished metal surface was then covered with a mask to expose a circular area of 0.3 cm^2 to the electrolyte. The electrolyte is a solution with 25 ppm chloride concentration and pH 6 at room temperature. This is to simulate the conditions found in packages embedded in epoxy mold compounds. For each experiment, 70 ml of electrolyte was prepared with deionized water and reagent-grade chemicals. The electrolyte was degassed with compressed nitrogen gas and stirred for 30 min prior to the start of each electrochemical experiment. In industrial humidity reliability tests, the epoxy mold compound usually contains less than 100 ppm chloride concentration and has a pH of around 4 to 7 [1, 2]. The migration of chloride towards the bond pad is enhanced by moisture absorption into the package. In our study, an electrolyte solution of pH 6 and chloride concentration of 25 ppm were chosen. The choice is justifiable since the samples are directly exposed to the electrolyte and hence less severe conditions could be used to simulate the actual package environment.

Electrochemical experiments were conducted using a conventional three electrode cell and results were registered using PCI4/300TM potentiostat with PHE200TM software (Gamry Instruments, Inc.). The metal/IMC sample was the working electrode while Pt was used as the counter electrode. Ag/AgCl electrode was used as a reference that has a potential of +0.197V vs. SHE. All experiments were conducted at ambient conditions of around $25 \pm 1^\circ\text{C}$. The distance between the working and reference electrode was kept between 3 to 5 mm to minimize ohmic drop across the electrodes. The electrochemical

experiments were conducted in sequential steps which include 1 hour of open circuit potential for the system to reach a steady state, followed by electrochemical impedance spectroscopy (EIS) and finally potentiodynamic polarization. The EIS experiments were conducted at the open circuit potential with an AC signal from 10 kHz to 10 mHz having an amplitude of 10 mV. Potentiodynamic polarization was conducted from a starting potential of -0.25 V vs open circuit potential (E_{oc}) to a final potential of +0.25 V vs E_{oc} at a scan rate of +1.0 mV/s. Electrochemical tests for each sample were conducted 3 times with a freshly grinded sample and fresh electrolyte each time. Echem Analyst 5.58TM software was used for plotting, graphing and fitting the data.

6.3 Results and Discussions

6.3.1 Composition and Crystal Structure

Cu and Cu-Al IMCs with different Pd concentrations (0, 3 and 10% weight replacement of Cu) were prepared by arc melting the metals in an argon gas environment to minimize oxidation. The nominal compositions of the samples are given in Table 6.1. The samples were cross-sectioned and an EDX point analysis was performed. Six points were used to check for sample homogeneity. The alloy samples exhibit quite good homogeneity based on SEM observation (Refer to Appendix Figure A.1), except that the Pd distribution in the Al-rich samples was not as uniform as the Cu-rich samples. Some Pd segregation was also observed at high Pd concentrations at 10 wt.% Pd. (Refer to Appendix Figure A.2). XRD analysis was then performed to ensure that the correct IMC phases were formed. The scanning angle ranges from $2\theta = 10$ to 100° . The desired IMC phase was present in all the samples except for the (Cu-10%Pd)Al₂ sample where a second Cu₃Al₂ phase was detected. The actual composition and crystal structure were reported in Chapter 5.

Table 6.1 Nominal composition of Cu and Cu-Al IMCs (wt.%)

	Cu (wt.%)	Al (wt.%)	Pd (wt.%)
Pd alloyed with Cu			
1. Cu	100	0	0
2. Cu-3%Pd	97.0	0	3
3. Cu-10%Pd	90.0	0	10
Pd alloyed with CuAl₂			
1. CuAl ₂	54.1	45.9	0
2. (Cu-3%Pd)Al ₂	52.5	45.9	1.6
3. (Cu-10%Pd)Al ₂	48.7	45.9	5.4
Pd alloyed with CuAl			
1. CuAl	70.2	29.8	0
2. (Cu-3%Pd)Al	68.1	29.8	2.1
3. (Cu-10%Pd)Al	63.2	29.8	7.0
Pd alloyed with Cu₉Al₄			
1. Cu ₉ Al ₄	84.1	15.9	0
2. (Cu-3%Pd) ₉ Al ₄	81.6	15.9	2.5
3. (Cu-10%Pd) ₉ Al ₄	75.7	15.9	8.4

6.3.2 Open Circuit Potential

When a metal is immersed in a given electrolyte, electrochemical reactions occur at the surface of the metal causing the metal to corrode. An electrochemical potential, called the open circuit potential, is created due to the reactions. The corrosion potential was allowed to stabilize to ensure that sufficient time had passed for the system to reach a steady state for reliable EIS and potentiodynamic polarization to be conducted. Figure 6.1 shows the time behavior of the corrosion potential of the metals and IMCs. The corrosion potential curves for all samples decreased with time before reaching a steady state value. The shift of the corrosion potential towards more negative values with time indicates that there is no passivation film inhibiting the corrosion and there is active dissolution of the metals and intermetallics in the electrolyte. Pure Al was observed to have the lowest open circuit potential and pure Cu the highest open circuit potential.

Figure 6.1 Open circuit potential vs time of various pure Cu, pure Al and Cu-Al IMCs in 25 ppm chloride solution at pH 6.

6.3.3 EIS

After the system has reached a steady state, electrochemical impedance spectroscopy (EIS) was employed to probe the impedance characteristics of the samples in the electrolyte. Figure 6.2 shows nyquist plots (imaginary part of impedance vs. real part of impedance at different frequencies) from EIS experiments of the samples in the electrolyte. All the impedance spectra were fitted to the proposed equivalent circuits. The proposed equivalent circuits for Cu and Cu₉Al₄ are shown in Figure 6.3. Pointers in Figure 6.2 correspond to experimental data and solid lines to theoretical predictions based on the equivalent circuit model. The proposed equivalent circuit models were able to fit the data quite well. As shown in Figure 6.2, the nyquist plot for pure Cu and Cu₉Al₄ IMC indicated one capacitive loop corresponding to a single charge transfer reaction. The shape of the impedance spectra for Cu is similar to those found in literature [4]. The shape of the Cu₉Al₄ impedance spectra is similar to pure Cu due to a significant percentage of Cu atoms in the IMC. The nyquist plot for CuAl, CuAl₂ and pure Al indicates two capacitive semicircles which suggest the presence of two time-constants corresponding to dissolution of the samples through two dissolution paths. For the CuAl

and CuAl_2 samples, the two dissolution processes should be due to both Cu and Al reactions. For pure Al, it could be due to the reactions from both aluminum and some aluminum oxides. The impedance spectra contain depressed circle with the centre under the real axis. This could be attributed to sample surface inhomogeneity and the presence of various crystal planes and grain boundaries giving rise to capacitance dispersion [5]. As shown in Figure 6.3, constant phase element (CPE) is used in place of a capacitor to compensate for inhomogeneity in the sample [6]. CPE is attached with their n values. When $n = 0$, the CPE is a resistor, while when $n = 1$, the CPE represents a perfect capacitor [7]. R_s is the uncompensated bulk solution resistance, R_{ct} is the charge transfer resistance of the corrosion reaction, R_{pf} is associated with absorbed inhibitors on the electrode which could be due to the corrosion products. The EIS parameters calculated from the proposed circuit model are shown in Table 6.2. A higher Zmodulus at low frequency indicates a better corrosion resistance. It is clearly seen that the impedance of the samples decrease in the order of $\text{Cu} > \text{CuAl} > \text{CuAl}_2 > \text{Cu}_9\text{Al}_4 > \text{Al}$. The charge transfer resistance, R_{ct} , for Cu is bigger than that for Cu_9Al_4 and is indicative that Cu is more resistant to corrosion than Cu_9Al_4 .

Figure 6.2 Nyquist plots from EIS experiments of pure Cu, pure Al and Cu-Al IMCs in 25 ppm chloride solution with pH 6.

Figure 6.3 Proposed equivalent circuit to model the behavior of Cu and Cu₉Al₄ in a 25 ppm chloride solution with pH 6.

Table 6.2 EIS parameters of the samples in 25 ppm chloride solution with pH 6

Samples	Pure Cu	Cu ₉ Al ₄
R_s (Ω)	1.15×10^3	908
R_{ct} (Ω)	1.81×10^3	722
CPE_1 (μF)	2.15	3.22
n_1 , dimensionless	0.32	0.26
R_{pf} (Ω)	2.34×10^7	4.49×10^5
CPE_2 (μF)	0.71	11.9
n_2 , dimensionless	0.94	0.75

6.3.4 Potentiodynamic Polarization

After the steady-state open circuit potential was reached, the potential was scanned from -0.25 V to +0.25 V with respect to the open circuit potential and the resulting current response measured. Figure 6.4 shows a comparison of the experimental potentiodynamic polarization curves of the samples. Corrosion currents (i_{corr}) and corrosion potential (E_{corr}) were obtained from the polarization curves by Tafel's extrapolation, using both cathodic and anodic branches of the polarization curves, and considering the potential ranging from +/-150 mV from open circuit potential. The results of the Tafel extrapolation of Figure 6.4 including the corrosion currents (i_{corr}) and corrosion potentials (E_{corr}) are presented in Table 6.3. These values are calculated from

the Tafel fit routine provided by Gamry Echem Analyst software. This routine uses a non-linear chi-squared minimization to fit the experimental data to the Butler-Volmer equation shown in Equation 6.1 [8]. The fitting quality of the data was estimated by the chi-square test. The chi-square values obtained for each Tafel fit is very small, which indicates the goodness of fit of the data is good. The individual value plot of the corrosion current of the samples was graphed using Minitab 15 Statistical software and shown in Figure 6.5.

$$i = i_{corr} \left[e^{2.303\eta/(\beta_a)} - e^{-2.303\eta/(\beta_c)} \right] \quad (6.1)$$

$$\eta = E - E_{corr} \quad (6.2)$$

- where i = the measured cell current in amperes
 i_{corr} = the corrosion current in amperes
 E = the electrode potential in volts
 E_{corr} = the corrosion potential in volts
 η = difference between the applied electrode potential and the corrosion potential
 β_a = the anodic Beta Tafel Constant in volts/decade
 β_c = the cathodic Beta Tafel Constant in volts/decade

As seen in Figure 6.4, both reduction and oxidation processes occur on the surface of all the samples. The cathodic process of the corrosion system should be attributed to the reduction of hydrogen ions in the solution since the solution is slightly acidic and H^+ ions exist [9]. There is no steep slope on the anodic branch of the polarization curve which shows that there is no passivation behavior inhibiting corrosion. As shown in Figure 6.5, the highest corrosion current, i_{corr} was observed for the Al and Cu_9Al_4 samples. The lowest corrosion currents were observed for the Cu samples. This can be explained by the ranking of Al and Cu in the electrochemical galvanic series, with Al having a more negative potential in the galvanic series which means that it will corrode more preferentially than Cu. In terms of the Cu-Al IMCs, Cu_9Al_4 exhibited the highest corrosion rate, followed by $CuAl_2$ and lastly $CuAl$. The corrosion susceptibility of the IMCs to chloride ions is observed to be independent of the concentration of Al in the IMCs. The trend observed in the corrosion rate of the IMCs could be due to the differences in binding energies of the IMCs which could affect the stability of the IMCs.

Breach et al. suggested a correlation between the surface energy and chemical stability of Cu-Al IMC. Cu_9Al_4 was calculated to have the highest surface energy and is the least stable [10].

From Figure 6.5 and Table 6.3, the addition of Pd results in slightly reduced corrosion current in the samples except for Cu_9Al_4 and CuAl_2 IMCs. This shows that Pd slightly improves the corrosion resistance of the samples. The results are expected since Pd is a noble metal and can provide enhanced corrosion resistance to the samples. For CuAl_2 samples, the corrosion current was observed to decrease with the addition of Pd up to 3 wt.%, then the corrosion current increases at 10 wt.% Pd addition. This can be explained by the presence of multiple phases in the $(\text{Cu-10\%Pd})\text{Al}_2$ sample which causes some localized corrosion due to more grain boundaries. In addition, galvanic corrosion can arise between the phases with different electrochemical potential giving rise to a higher corrosion rate [11]. For the Cu_9Al_4 samples, there is no significant effect seen from the addition of Pd. This could be due to the large variations in the measured corrosion current among the samples. The corrosion potential, E_{corr} was observed to be most negative for Al and most positive for Cu. For the IMCs, the absolute value of the corrosion potential is in the order $\text{CuAl}_2 > \text{CuAl} > \text{Cu}_9\text{Al}_4$. The data trend is in good agreement with the open circuit potential values discussed earlier. A more negative corrosion potential indicates that the sample is more prone to corrosion as the anodic corrosion rate is higher, releasing more electrons [12]. However, the corrosion potential for Cu_9Al_4 is not very negative and it can be due to alloying effects.

The overall results show Pd provides a slight improvement to the corrosion resistance of the Cu metal and Cu-Al IMCs. This agrees well with reliability test performed by Qin et al. which shows Pd-Cu wire bonds performing better than bare Cu bonds in industrial molded HAST test [13]. Hence, Pd-Cu wire bonds are expected to perform better in a humidity reliability test with halogen-containing epoxy mold compound at different annealing durations. From the results, it was shown that the Cu-Al IMCs are much more prone to corrosion than pure Cu. Reliability of copper wire bonds in humid conditions is expected to decrease with thermal annealing due to the formation of more corrosion prone IMCs. Cu_9Al_4 is observed to be the IMC with the highest corrosion current in the acidic chloride solution and is most prone to corrosion. This is in agreement

with reported literature that Cu_9Al_4 is the IMC layer that corrodes during molded reliability tests such as HAST and PCT [2, 14]. It was reported that in thermal aging of the copper wire bonds, Cu_9Al_4 appears as a second IMC between CuAl_2 and the copper bond. CuAl_2 is the dominant phase until the Al pad is depleted. After which, CuAl_2 begins to transform to Cu_9Al_4 and the latter is the dominant phase due to the excess supply of Cu. At this stage, the reliability of the wire bonds will be expected to drop significantly. Hence, a thicker Al pad will be beneficial to the reliability of copper wire bonds.

An EDX point analysis was made on the IMC samples after potentiodynamic polarization test to identify possible corrosion products (Figures 6.6 to 6.8). For all the IMC samples, a thin brownish film of corrosion material was observed. For Cu_9Al_4 IMC with the highest corrosion rate, corrosion products were observable as shown in Figure 6.6b. In addition, as shown in Figure 6.6c, a high amount of oxygen was detected. The corrosion particles have a much higher Al content than Cu_9Al_4 . This suggests that the corrosion products may include aluminum-based oxides. Chlorine was also detected on the sample, which should be from the electrolyte solution. No corrosion residues were observed on CuAl_2 and CuAl samples. EDX analysis was performed on the surface of the corroded samples. Cu, Al, and much smaller amount of O were detected as shown in Figure 6.7 and 6.8. Some pin holes were found on the samples after the electrochemical test.

Figure 6.4 Potentiodynamic polarization curves for Cu, Al and Cu-Al IMCs in 25 ppm chloride solution with pH 6.

Figure 6.5 Effect of Pd on the corrosion current of Cu, Al and IMCs. Red dot (●) represents the corrosion current of individual measurement. Blue ⊕ symbol represents mean value of three measurements.

Table 6.3 Potentiodynamic Polarization response of Cu, Al and Cu-Al IMCs.

Samples	$i_{\text{corr}}(\text{nA})$	$E_{\text{corr}}(\text{mV})$	<i>Chi Squared</i>
Pure Cu	33.4 ± 14	-91.3 ± 50	0.049
Cu-3%Pd	26.8 ± 4	-147 ± 77	0.054
Cu-10%Pd	21.6 ± 5	-137 ± 68	0.092
Cu ₉ Al ₄	826 ± 324	-238 ± 59	0.122
(Cu-3%Pd) ₉ Al ₄	720 ± 107	-224 ± 107	0.110
(Cu-10%Pd) ₉ Al ₄	866 ± 184	-151 ± 55	0.149
CuAl	371 ± 123	-776 ± 25	0.090
(Cu-3%Pd)Al	201 ± 81	-729 ± 32	0.063
(Cu-10%Pd)Al	109 ± 28	-483 ± 33	0.040
CuAl ₂	559 ± 96	-879 ± 9	0.069
(Cu-3%Pd)Al ₂	271 ± 196	-859 ± 72	0.093

(Cu-10%Pd)Al ₂	245 ± 156	-909 ± 34	0.105
Pure Al	1068 ± 182	-909 ± 100	0.126

Figure 6.6 (a) SEM image of (Cu-3%Pd)₉Al₄ before experiment (b) Corrosion product found on the sample after electrochemical test and (c) EDX spectrum of the corrosion products

Figure 6.7 (a) SEM image of CuAl₂ before experiment (b) Corrosion film on the sample after electrochemical test and (c) EDX spectrum of the corrosion product

Figure 6.8 (a) SEM image of CuAl before experiment (b) Corrosion film on the sample after electrochemical test and (c) EDX spectrum of the corrosion product

6.4 Conclusions

A systematic study on the corrosion characteristics and corrosion resistance of Cu, Al and Cu-Al IMCs (namely CuAl_2 , CuAl and Cu_9Al_4) in 25 ppm chloride solution with pH 6 was studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. The electrochemical test of the individual metals and alloys in the chloride medium were performed to provide a pure environment for the corrosion test, eliminating effects from other factors such as the bonding wire quality, wire bonding parameters, Al pad profile, the consistency of the properties of the epoxy mold compound etc. which might affect the corrosion rate. The findings provide important information for the long term reliability of Cu wire bonded packages. The following conclusions can be made based on the investigations:

1. The electrical impedance of the samples in the acidic chloride solution is in the order of $\text{Cu} > \text{CuAl} > \text{CuAl}_2 > \text{Cu}_9\text{Al}_4 > \text{pure Al}$. Corrosion current for the metals and IMCs follow the order $\text{Al} > \text{Cu}_9\text{Al}_4 > \text{CuAl}_2 > \text{CuAl} > \text{Cu}$.
2. The observed increase in corrosion current among different IMCs is in accordance to the decreasing impedance.
3. The addition of Pd was shown to slightly improve the corrosion resistance of the Cu and CuAl samples in chloride medium. For Cu_9Al_4 samples, not much effect from Pd can be seen which could be due to the large variation in the measured data.

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Chapter 7

Interfacial Evolution and Bond Reliability in Pd-Cu Wire Bonds

In this chapter, the growth kinetics of Cu-Al intermetallic compounds formed during isothermal annealing of Pd-Cu wire bonds with different palladium distribution at 175°C are investigated by electron microscopy and compared to bare Cu wire bonds. Transmission electron microscopy (TEM) was used to provide high resolution imaging of the Cu-Al IMCs in the as-bonded state and TEM-EDX used to analyze the concentrations of Pd at the bond interface in the as-bonded state. Cu-Al IMCs were found to grow thicker with increasing annealing duration. The growth kinetics of the Cu-Al IMCs was correlated with the diffusion process during thermal annealing. The IMC thickness for Pd-Cu wire bonds with Pd at the bond interface was found to be thinner as compared to that for Pd-Cu wire bonds with no Pd at the bond interface. Thus the presence of palladium at the bond interface has slowed down the IMC growth. Nano voids were found in the Pd-Cu wire bonds with Pd at the bond interface but not in the Pd-Cu wire bonds with no Pd at the bond interface. The IMC growth rate for the Pd-Cu bonds with no Pd was found to be close to that for bare Cu for the initial annealing durations. Corresponding bond pull test showed that Pd-Cu wire bonds containing Pd have best preserved the bond strength after 168 h aging at 175 °C due to the beneficial presence of Pd.

7.1 Introduction

Optimal IMC coverage and growth can lead to enhanced wire bond strength and reliability. However, excessive formation of IMCs and voids during thermal annealing can significantly impact the strength and reliability of the wire bonds. In Chapter 4, it has been shown that it is possible to vary the palladium distribution in the Pd-Cu bonded ball by adjusting the electronic flame off (EFO) current during the free air ball formation process where the wire is being melted to form a ball. High EFO current results in the absence of Pd on the bond interface while a low EFO current gives rise to a Pd-rich layer at the bond interface. The different Pd distribution in the bonded ball result in varying concentrations of palladium at the wire bond interface which can affect Cu-Al IMC growth during thermal annealing. To date, a comparison of the growth kinetics of Cu-Al IMCs and bond reliability of Pd-Cu wire bonds with different palladium distribution has not been reported.

In this chapter, the effect of thermal annealing on the interfacial evolution of Cu-Al IMCs was investigated using Pd-Cu wire bonds with and without the presence of a Pd-rich layer at the bond interface. The wire bonds were annealed at 175°C in nitrogen ambient to reduce oxidation of the wire bonds and the bond interfacial structure studied as a function of annealing time. The interfacial morphology of the wire bonds on aluminum metallization pad and the growth kinetics of Cu-Al IMCs were also examined. The un-molded bond reliability of the Pd-Cu wire bonds with different Pd distributions was analyzed by studying the process responses at various annealing durations. In all these tests, bare Cu is used as a baseline for comparison.

7.2 Experimental Methods

In this study, 0.6 mil (15 μm) Cu and Pd-Cu wires were bonded to an aluminum metallization with a thickness of approximately 1 μm attached to a ball grid array (BGA) substrate by employing a Kulicke & Soffa (K&S) IConn ProCu^{PS} automatic ball bonder. The wire bonding setup and parameters have been provided in Section 3.1.

The electronic flame off (EFO) current was varied to produce Pd-Cu bonds with

the following conditions: 1) Pd-Cu wire bonds with the presence of a Pd-rich layer at the bond interface 2) Pd-Cu wire bonds with no Pd at the bond interface and 3) bare Cu wire bonds as a baseline for comparison. An optimized set of process parameters involving contact velocity (CV), ultrasonic current (USG) and bond force was used to ensure a bonded ball size of 27 μm and a ball height of 7 μm . Process responses such as ball diameter, ball height, ball shear, IMC coverage, first bond pull and aluminum pad splash in the USG vibration direction were measured. For the first bond pull test, the wire is pulled at the top of loop near the first bond region. A sample size of 20 bonded balls was used for all the measurements. To accelerate the interfacial evolution of Cu-Al to study the growth kinetics, the wire bonds were annealed at 175°C for 24 h, 48 h and 168 h in an oven in nitrogen ambient to reduce oxidation on the wire bonds.

After thermal annealing, the Pd-Cu and bare Cu wire bonds were cross-sectioned using a FEI dual beam focused ion beam (FIB) system for observation of IMC growth under SEM. The IMC area was analyzed using the imaging software Image-J, version 1.49. The average thickness of the IMCs at different annealing durations was calculated by dividing the overall IMC area by the wire bond diameter. Electron transparent films of selected samples for TEM analysis were prepared using the FIB lift-out technique. TEM was used due to the nanoscale IMC structure present in the as-bonded state which could not be easily identified with a SEM. A molybdenum (Mo) grid was used for supporting the TEM samples to avoid EDX peak overlaps with the copper wire bonds. TEM was performed at 200kV using a FEI Titan 80-300 TEM. A microprobe beam was used for EDX elemental analysis in scanning transmission (STEM) mode.

7.3 Results and Discussion

7.3.1 Effect of Pd Distribution on the First Bond Process Responses

The first bond process windows were obtained based on the same procedure as described in Chapter 4. At these parameter settings, all the wire bonds break at the ball neck as shown in Figure 7.1. From Figure 7.2, it is seen that the size of the process window is similar for all the sample conditions except for the Pd-Cu sample with no Pd at the bond interface. A 20% process window was obtained for the Pd-Cu wire bonds with a

Pd-rich layer at the bond interface and the bare Cu wire bonds, while a 15% process window was obtained for the Pd-Cu wire bonds with no Pd at the bond interface. The smaller process window obtained for the Pd-Cu wire bonds with no Pd could be due to the very high EFO setting used to form the FAB. At very high EFO current settings, Cu flows out at a faster rate due to the steeper temperature gradient. This results in turbulent flow of Cu and partial melting of Pd causing a random distribution of Pd within the FAB bulk. This results in a larger variation in the FAB hardness and smaller process window. The process windows for the Pd-Cu bonds were shifted to the right compared to the bare Cu wire bonds. This could be due to a slightly harder Pd-Cu FAB compared to the bare Cu FAB which requires slightly heavier process parameters for good adhesion to the bond pad.

A set of measurements such as ball diameter, ball height, aluminum splash in the Y-direction, shear per area, IMC coverage and first bond pull were collected and are presented in Table 7.1. As shown in Table 7.1, the mean pull value for Pd-Cu wire bonds is about 1g higher than that for bare Cu wire. This is due to the higher tensile strength of the Pd-Cu wire compared to the bare Cu wire. The Al pad splash for Pd-Cu wire bonds is bigger than that for bare Cu wire. This is due to the heavier first bond process parameters used to bond the harder Pd-Cu FAB. The result is consistent with previous study which revealed a larger Al splash with Pd-Cu wire [1]. There is no significant difference in first bond process responses among the Pd-Cu wire bonds with different Pd distributions.

The samples were then annealed at 175°C for different times and pull tests performed. The results for pull strength and peeling rate at different annealing durations are shown in Table 7.2 and the box plots shown in Figure 7.3. As seen from Table 7.2, for all the samples, the pull strength decreases and pad peels increase with longer annealing time. This is due to the growth of IMCs with time which causes irregular volumetric increases, resulting in stress build up on the aluminum metallization giving more pad peels. A similar finding was reported by Qin et al. where pad peels appear after long ageing durations of Cu wire bonds [2]. Comparing among the Pd-Cu wire samples, the pull values for Pd-Cu bonds with no Pd at the bond interface drops and the percent (%) pad peels increases more drastically compared to that for Pd-Cu bonds with Pd-rich layer at the bond interface. Further discussion of this phenomenon will be made in Section

7.3.3 of the paper. Figure 7.3 shows that Pd-Cu bonds with absence of Pd at the interface demonstrates the greatest variability in the pull strength. This could be due to the random distribution of Pd in the wire bond which results in variation in hardness. The median pull values were also seen to drop more drastically compared to Pd-Cu bond with Pd at the bond interface.

A paired T-test was performed to check if there is a significant difference between the mean pull values of the two Pd-Cu samples, using a confidence level of 95%. From Table 7.3, at 0 and 24 h of annealing, there is no significant difference in the mean pull strengths between the two Pd-Cu wire bond conditions as indicated by the high P-value. At 48 h and 168 h of annealing, the pull value for the Pd-Cu sample at low EFO current is significantly higher than that for the high EFO current. The difference between the sample means is 0.53g and 0.79g at 48 h and 168 h respectively. The statistical significance (2 tailed *p*-value) of the paired t-test (P value) obtained was 0.003 and 0 at 48 h and 168 h respectively. As the *p*-value is less than 0.05, it can be concluded that there is statistically significant difference between pull strengths at the two annealing time points (48 h and 168 h).

Figure 7.1 Wire bonds broken at the neck after the first bond pull indicating good bondability.

Figure 7.2 Process windows for bare Cu and Pd-Cu bonds with different Pd distributions in the as-bonded state.

Table 7.1 First bond process response for bare Cu and Pd-Cu bonds in the as-bonded state.

Process Response	Pd-Cu (Optimized Low EFO current)	Pd-Cu (High EFO Current)	Bare Cu
Ball Diameter (μm)	27.63	27.90	27.20
Ball Height (μm)	7.56	7.43	7.31
Aluminum Splash(μm)	32.27	32.51	31.75
Shear force (g)	8.54	8.71	8.83
Shear/Area (g/mil^2)	9.2	9.2	9.1
IMC (%)	91.5	91.3	92.4
Pull Average (g)	5.59	5.73	4.74
Pull Min (g)	5.10	5.14	4.12

Table 7.2 First bond pull strength and pad peels % after thermal annealing at 175°C.

Pd-Cu (presence of Pd at bond interface)	0 h	24 h	48 h	168 h
Pull Average (g)	5.59	5.44	5.30	4.88
Pull Min (g)	5.10	5.03	4.82	4.27

Stdev	0.20	0.40	0.43	0.46
Peels %	0	1.6	4.6	12.6
Pd-Cu (absence of Pd at bond interface)				
Pull Average (g)	5.73	5.49	4.80	3.92
Pull Min (g)	5.14	4.88	3.92	3.31
Stdev	0.20	0.43	0.73	0.65
Peels %	0	3.6	10.6	20.5
Bare Cu				
Pull Average (g)	4.74	4.32	4.20	3.80
Pull Min (g)	4.12	3.88	3.52	3.14
Stdev	0.26	0.3	0.49	0.48
Peels %	0	1.2	5.2	14.7

Figure 7.3 Box plot of first bond pull strength in the as-bonded state and after annealing. Black $\oplus$ symbol represents the median value of the measurements.

Table 7.3 T-test results of the pull values for Pd-Cu samples

Pull value (g)	Annealing time (h)	Pd-Cu (Low EFO current)		Pd-Cu (High EFO current)		95% CI for Mean	T-value	P-value
		Mean	SD	Mean	SD			
	0	5.6159	0.208	5.6424	0.306	-0.2152,	-0.28	0.781
	24	5.5184	0.2426	5.4438	0.3208	-0.139,	0.73	0.475
	48	5.342	0.337	4.812	0.601	0.202,	3.39	0.003
	168	4.942	0.415	4.156	0.521	0.532,	6.47	0

7.3.2 Effect of Pd Distribution on the Interfacial Morphology and IMC Formation in the As-bonded State

EDX line scan using STEM were performed on the cross-sectioned Pd-Cu bonds in the as-bonded state to verify the concentrations of palladium at the bond interface for the Pd-Cu samples. Figures 7.4 and 7.5 show the EDX line scan results. As shown in Figure 7.4a, for the Pd-Cu sample with presence of Pd, about 5 at.% Pd was detected at the bond periphery and in Figure 7.4b, ~3 at.% Pd was detected in the central interface. As seen in Figure 7.5, for the Pd-Cu sample with no Pd at the bond interface, the Pd signal based on EDX line scan is nearly zero for both the bond periphery and bond center which confirms that Pd is absent at the bond interface. For both of these samples, Pd is not present in the IMC based on the EDX line scan.

Due to the nano-scale structure of the IMC in the as-bonded state, high-angle annular dark-field (HAADF) STEM was employed to study the wire bonds morphology and IMC thickness of the wire bonds before thermal annealing. For HAADF STEM, the image intensity increases with both atomic number and sample thickness, so for sample areas with approximately constant thickness the heavier elements (e.g., Cu) appear brighter. Images of the bond interface in the as-bonded state are shown in Figure 7.6. Based on Figure 7.6a showing the Pd-rich sample, numerous nano voids were observed on the wire bonds concentrated at the bond interface. These are the areas where EDX shows the presence of Pd and it can be seen that nano voids are strongly related to the presence of Pd. The presence of voids in the as-bonded state suggests that they could have been formed during the FAB formation process and a possible cause was given early

in Chapter 4. The presence of nano voids has no significant effect on the bond reliability based on the first bond pull strength results. As seen in Figure 7.6b, no nanovoids were observed on the Pd-Cu sample containing no Pd at the bond interface. For both the Pd-Cu samples, island-like IMC particles were found at the bond interface in the as-bonded state. Diffraction pattern (Figure 7.7) was collected from the IMC region and was found to have a crystal structure of CuAl_2 [210] ($I4/mcm$, $a = 6.067\text{\AA}$), with a good agreement to the EDX results. CuAl_2 was reported to be the IMC formed in the as-bonded state for both Cu and Pd-Cu wires [3-5]. The IMC was also seen to grow towards the Al pad, which indicates that Cu diffuses into the Al pad during the annealing process. The presence of IMC in the as-bonded state is due to the inevitable heating of the wire bonds in the heated workholder during bonding. The IMC thickness in the as-bonded state is around ~ 20 nm.

Figure 7.4 EDX line scan across (a) the peripheral and (b) the central parts of the Pd-Cu bond with Pd at bond interface in the as-bonded state. In the corresponding elemental distribution plot on the right, the red, green, and blue lines indicate Pd, Al, and Cu concentrations, respectively.

Figure 7.5 EDX line scan across (a) the peripheral and (b) the centre of the Pd-Cu bond with no Pd at bond interface in the as-bonded state. In the corresponding elemental distribution plot on the right, the red, green, and blue lines indicate Pd, Al, and Cu concentrations, respectively.

Figure 7.6 HAADF STEM images of (a) the Pd-Cu bond containing Pd showing nano voids in the Cu (dark spots) and (b) the Pd-Cu bond with no Pd.

Figure 7.7 Diffraction pattern of the CuAl_2 IMC in the as-bonded state.

7.3.3 Effect of Pd Distribution on the Interfacial Morphology during Thermal Annealing

The Pd-Cu and bare Cu wire bonds were annealed for 24 h, 48 h and 168 h to study their growth behavior. Thermal annealing results in the growth of IMCs in Cu-Al bonds which leads to morphology changes and an increase in IMC thickness. Two samples were cross-sectioned for each setting to ensure repeatability of the results. Cross-sectional SEM images of the wire bonds after different annealing durations are shown in Figures 7.8 to 7.10. In the as-bonded state, the IMC is too thin to be visible under SEM, hence TEM was employed to study the nanoscale structure (as discussed in Section 7.3.2). After 24 h of annealing, two layers of IMCs are observed in all the samples.

The IMCs for the Pd-rich sample were observed to grow more slowly than the other samples, reaching ~230 nm compared to ~260 nm for the Pd-Cu sample with no Pd at the interface and ~265 nm for the bare Cu sample. After 168 h of annealing, the total IMC thickness for the Pd-Cu sample with Pd presence was ~423 nm compared to ~450 nm and ~498 nm for the other Pd-Cu and the bare Cu sample respectively. The presence of Pd at the bond interface was shown to significantly reduce the Cu-Al IMC growth. This is due to the presence of Pd atoms at the bond interface which impedes the diffusion of Cu atoms through the Cu-Al IMCs. The IMC thickness for the Pd-Cu sample with no

Pd in the as-bonded state was observed to be close to that for bare Cu sample at the initial annealing stage, deviating from it only at longer annealing durations. This could be due to the diffusion of Pd to the bond interface after longer annealing times, which slows down the growth of Cu-Al IMCs. In another study, Pd was also observed to diffuse towards the bond interface with thermal annealing [2, 5].

As shown in Figure 7.9, after 24 h of annealing, some cavities were present near the edge of the bond of the Pd-Cu sample with no Pd in the as-bonded state. The presence of voids could account for the drastically lower pull strength of the bonds after 24 h of annealing as discussed in Section 7.3.1. In addition, the faster interface reaction as indicated by a faster IMC reaction compared to the sample containing Pd may have also contributed to the weakening of the interface, resulting in more pad peels and degradation of the bonds.

In a solid state reaction, the growth of intermetallic compounds at the interface between two dissimilar metals at ageing time t is often expressed by the following equation [6]:

$$x - x_0 = (Kt)^{\frac{1}{n}} \quad (7.1)$$

where x is the IMC thickness after annealing time, t

x_0 is the initial IMC thickness at $t = 0$, in our case $x_0 = 20$ nm

t is the annealing duration

K is the growth rate constant

n is the time exponent

Figure 7.11 shows a plot of the total Cu-Al IMCs thickness as a function of annealing durations. Table 7.4 shows numerical values of the total Cu-Al IMCs thickness after different annealing durations. Figure 7.12 shows the thickness of the IMC layers as a function of the square root of the annealing time. Based on Figure 7.11, the total thickness of the IMCs was observed to follow a parabolic law and from Figure 7.12, the total thickness of the IMCs was found to increase linearly with the square root of annealing duration. This shows that the IMC growth follows a parabolic equation where $n = 2$, and is a diffusion controlled process. This is similar to bare Cu wire bonds where Xu et al. reported a diffusion controlled process [7]. The regression fitting of the

experimental results with Equation 7.1 is summarized in Table 7.5. As shown in Table 7.5, the regressed n values for all the samples are very close to 2, which further confirms that the IMC growth rate for both Pd-Cu and bare Cu wire bonds can be described by diffusion controlled process. The R squared value is an indication of how well the data fits the model. From Table 7.5, the R squared values are high which indicates that there is a good fit of the experimental data.

Figure 7.8 Cross-sectional SEM images of Pd-Cu wire bonds with Pd at the bond interface in the as-bonded state after annealing at 175°C for: (a) 0 h (b) 24 h (c) 48 h and (d) 168 h.

Figure 7.9 Cross-sectional SEM images of Pd-Cu wire bonds with no Pd at the bond interface in the as-bonded state after annealing at 175°C for: (a) 0 h (b) 24 h (c) 48 h and (d) 168 h.

Figure 7.10 Cross-sectional SEM images of bare Cu wire bonds after annealing at 175°C for: (a) 0 h (b) 24 h (c) 48 h and (d) 168 h.

Figure 7.11 Cu-Al IMC growth as a function of annealing duration for Pd-Cu and bare Cu wire bonds.

Table 7.4 Total IMC thickness after various annealing durations for Pd-Cu and bare Cu wire bonds

Ageing time(h) Sample	Pd-Cu (presence Pd at bond interface)			Pd-Cu (absence of Pd at bond interface)			Bare Cu		
	No. 1	No. 2	Average	No. 1	No. 2	Average	No. 1	No. 2	Average
0	20 nm	20 nm	20 nm	20 nm	20 nm	20 nm	20 nm	20 nm	20 nm
24	187 nm	183 nm	185 nm	200 nm	196 nm	198 nm	210 nm	205 nm	208 nm
48	230 nm	232 nm	231 nm	260 nm	261 nm	261 nm	265 nm	272 nm	269 nm
168	421 nm	425 nm	423 nm	467 nm	473 nm	470 nm	498 nm	504 nm	501 nm

Table 7.5 Regression values and n values for Pd-Cu and bare Cu wire bonds

Sample	R squared	<i>n</i>
Pd-Cu (presence of Pd at bond interface)	0.989	2.17
Pd-Cu (absence of Pd at bond interface)	0.998	2.12
Bare Cu	0.992	2.08

Figure 7.12 Cu-Al IMC growth vs square root of annealing durations.

7.4 Conclusions

This chapter investigates the effect of palladium distribution on the bondability, interfacial evolution, and reliability of Pd-Cu bonds on Al metallization. Bare Cu wire was used as a baseline for comparison. The main conclusions from this study are as follows:

1. Around 3 to 5 atm. % of Pd was found on the bond interface of the Pd-rich Pd-Cu sample in the as-bonded state. Nano voids were also found at the bond interface and are related to the presence of palladium. The nano voids were found to have no influence on the first bond pull strength based on the pull results.
2. A smaller process window was obtained for the Pd-Cu wire bonds with absence of Pd at the bond interface in the as-bonded state. This could be due to the very high EFO setting used to form the free air ball which results in turbulent flow of Cu and partial

- melting of Pd causing random distribution of Pd within the FAB bulk. This results in a larger variation in the FAB hardness and smaller process window.
3. The presence of Pd at the bond interface significantly slows down the Cu-Al IMC growth during thermal annealing. The Pd atoms present in the Cu wire bond impedes the diffusion of the Cu atoms through the IMC layers.
 4. With long thermal annealing durations, large cavities were found on the bond edge of the Pd-Cu sample with absence of Pd in the as-bonded state. The pull strength was also observed to decrease and pad peels increased drastically with thermal annealing.
 5. The presence of Pd at the bond interface has a beneficial effect as it can best preserve the bond strength after the long-term annealing.

The findings provide important information on the effect of Pd distribution on the long-term reliability of Pd-Cu wire bonded packages.

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Chapter 8

Conclusions and Future Work

Through investigating the effect of palladium on the bondability, interfacial characteristics and reliability of Pd-Cu wire bonds, this thesis has addressed the knowledge gaps raised in thermosonic ball bonding using Pd-Cu wire. It was observed that process parameters such as the EFO current has a significant effect on the melting of the palladium and copper in Pd-Cu wires and subsequently affects the palladium distribution in Pd-Cu FABs. The hardness of the Pd-Cu FABs is dependent on the EFO current and palladium distribution. The mechanical properties of Cu and Cu-Al IMCs with addition of palladium were investigated using nanoindentation. Cu-Al IMCs was found to be harder and stiffer than pure Cu. The addition of a few percent of Pd slightly increases the hardness of the Cu and Cu-Al IMCs. The electrochemical test results revealed Cu_9Al_4 has the highest corrosion rate followed by CuAl_2 and CuAl . The thermal annealing test reveals that the presence of Pd at the bond interface helps to slow down the growth of Cu-Al IMCs, improving the long term reliability of Pd-Cu wire bonds. Implications and guidelines for bonding Pd-Cu wires and improving bond reliability are given based on the generated understandings of the thesis work.

8.1 Conclusions

This research project was set out to bridge the knowledge gaps between thermosonic bonding of Pd-Cu and bare Cu wire. Key questions such as the effect of palladium on the bondability, IMC growth and corrosion performance of Cu wire bonds on Al metallization has been addressed. In this thesis, the findings and novelties are as follows:

Effect of key process parameters on Pd distribution in Pd-Cu bonds

- Electronic flame off (EFO) current strongly affects the melting of the palladium layer and copper core in Pd-Cu wire and subsequently affects the palladium distribution in the FAB. At low EFO current, a thin uniform ring of Pd rich layer is found around the FAB peripheral, with Pd found at the FAB tip. At mid EFO current, the Pd rich phase mostly concentrates around the FAB neck region. At very high EFO current, there is a steeper temperature gradient, causing Cu to flow out at a faster rate. Turbulent flow of Cu and partial melting of Pd caused random distribution of Pd in the FAB bulk.
- At different EFO currents, the grain structure of copper core in Pd-Cu FAB remains similar, and the hardness of Pd-Cu FAB is mainly affected by the palladium distribution in the FAB. This is reflected in the on-bonder squash measurement which shows that EFO current has no effect on bare Cu FAB hardness, but affects the hardness of Pd-Cu FAB. Thus for Pd-Cu wire, the FAB hardness can be controlled by varying the EFO current. A low EFO current produced a slightly harder FAB compared to mid EFO current due to the presence of Pd at the FAB tip.
- The results based on this study allows two conditions of Pd-Cu FAB to be prepared for further investigation on the effect of palladium presence at the bond interface on the bondability, corrosion performance and IMC formation of the wire bonds.

Effect of palladium on the mechanical properties of Cu and Cu-Al intermetallic compounds

- The Cu-Al IMCs analyzed in this study exhibit much higher hardness and stiffness values than pure Cu. Hence, pad peels and pad cracks are expected to increase with prolonged thermal annealing of Cu wire bonds due to large volumetric growth of Cu-Al IMCs which causes stress build up in the underlying pad layers.
- Among all Cu-Al IMCs evaluated, CuAl exhibits the highest hardness and modulus while CuAl₂ possesses the lowest modulus and hardness.
- Pd slightly increases the hardness and stiffness of Cu and Cu-Al IMCs such as Cu₉Al₄, CuAl and CuAl₂ for up to 3 wt. % replacement of Cu. With further increase of Pd up to 10 wt. %, the modulus and hardness of the specimens are slightly reduced due to some Pd segregations. The hardness and modulus of these Cu-Al IMCs with Pd additions has not been reported before in literature.
- As Pd addition does not lead to large increases in Cu wire hardness, the bonding force required for Pd-Cu wire would not be significantly higher than that for bare Cu.

Evaluation of the corrosion performance of Cu-Al intermetallic compounds and the effect of palladium addition

- The corrosion performance of individual Cu-Al IMCs in an electrochemical cell has been investigated. Testing of the individual metals and IMCs provides a pure environment for the corrosion test, eliminating effects from other factors such as the bonding wire quality, wire bonding parameters, Al pad profile, the consistency of the properties of the epoxy mold compound etc. which might affect the corrosion rate.
- All the Cu-Al IMCs investigated have a higher corrosion current than pure Cu in an acidic chloride medium and hence has a higher propensity to corrode. This explains the results reported in industrial humidity reliability tests where the corrosion susceptibility and failure rate of Pd-Cu and bare Cu wire bonds increased at prolonged test durations.
- Based on electrochemical impedance spectroscopy results, the electrical impedance of the metals and Cu-Al IMCs decreases in the order: Cu > CuAl > CuAl₂ > Cu₉Al₄ > Al. Corrosion current for the metals and Cu-Al IMCs decreases in the order Al > Cu₉Al₄ > CuAl₂ > CuAl > Cu. In molded industrial humidity reliability tests, the wire bonded

devices will be expected to fail at a higher rate when Cu_9Al_4 are formed.

- Addition of palladium in concentrations of up to 10 wt. % as investigated in this study helps to slightly improve the corrosion resistance of Cu and Cu-Al IMCs in acidic chloride medium. Hence, Pd-Cu wire bonds would perform better in molded humidity reliability tests than bare Cu wire bonds in the as-bonded state and after prolonged reliability test durations.

Interfacial evolution and bond reliability in thermosonic Pd coated Cu wire bonding on aluminum metallization: Effect of palladium distribution

- Around 3 to 5 atm. % of Pd will be present at the bond interface of the Pd-rich Pd-Cu sample under low EFO condition. Nano voids are present at the bond because of the palladium distribution. However, the nano voids have no influence on the wire bondability based on the pull and shear results.
- The presence of Pd at the bond interface significantly slows down the Cu-Al IMC growth during thermal annealing. The total IMCs for the Pd-rich sample grow more slowly than the samples with no Pd at the bond interface, which indicates that Pd impedes the diffusion of the Cu atoms through the IMC layers.
- The growth of Cu-Al IMCs in Pd-Cu and bare Cu wire bonds follows a parabolic growth rate and is a diffusion controlled process.
- With long durations of thermal annealing, the pull strength of wire bond will inevitably decrease as a consequence of increased interface diffusion. Segregation of Pd at the bond interface therefore would bring in beneficial effect for the long-term reliability. Accordingly, a lower EFO current is preferred from package reliability point of view.

8.2 Implications and Guidelines

The findings from this study enable us to draw a number of key conclusions pertaining to the results sections; these are examined below.

8.2.1 Bondability

Based on the nanoindentation test results on the bulk Cu and Cu-Al IMCs, Pd slightly increases the hardness and stiffness of Cu and Cu-Al IMCs. This is also further verified using the on-bonder squash measurement technique, that Pd-Cu FAB is slightly harder than the bare Cu FAB. This is reflected in the process response and process windows, where only slightly heavier parameters are used for Pd-Cu wire bonding compared to bare Cu. Hence, the process parameters do not have to be adjusted significantly to cater to Pd-Cu wire bonding. This slight difference in hardness could be due to the thin Pd layer of 70 nm coated on the Cu core of the Pd-Cu wire. With larger wire diameters, the Pd coating will be thicker, and it is expected that there will be a bigger variation in the process parameters (such as force and USG) required for Pd-Cu wire bonding compared to bare Cu wire. Comparing among Pd-Cu FABs formed at different EFO currents, Pd-Cu FAB formed at low EFO current is only slightly harder than that formed at higher EFO currents based on the on-bonder squash measurement results. In terms of the bondability between Pd-Cu wire bonds with different Pd distributions, the process windows obtained are almost similar in size. This can be related to the slight difference in hardness among the Pd-Cu bonds formed with varying EFO parameter settings.

8.2.2 Intermetallic evolution and thermal reliability

The growth of Cu-Al IMCs during thermal annealing of Pd-Cu wire bonds with different Pd distributions has been studied and the results compared to bare Cu. Presence of Pd rich layer at the bond interface helps to reduce the IMC growth during thermal annealing. IMC formation and associated voids and cavities at the bond interface determine the strength and reliability of wire bonds. Optimal IMC formation is an indication of good weld and bondability. However excessive IMC growth causes adverse effects on the mechanical properties of the wire bonds and degrades bonds reliability during long term service. Hence, presence of palladium at the bond interface would help to preserve the thermal reliability of the wire bonds.

In the study, it was observed that Pd is not present in the Al rich IMC particles formed in the as-bonded state. More investigations were carried out to trace the behavior of Pd during the thermal annealing process. Figure 8.1 shows the EDX line analysis of Pd-Cu bond with Pd at bond interface after 24 h of annealing. From the line scan results, Pd is located in the copper rich IMC layer and the ball but not in the Al rich IMC layer. More TEM work needs to be done to trace the migration of Pd through the bond interface and to explain why Pd is only present in the copper rich IMC but does not penetrate into the Al rich IMC.

Figure 8.1 EDX line scan across (a) the peripheral and (b) the center of the Pd-Cu bond with Pd at bond interface after 24 h annealing. In the corresponding elemental distribution plot on the right, the red, green, and blue lines indicate Pd, Al, and Cu concentrations, respectively.

8.2.3 Molded Humidity Reliability

The corrosion performance of Cu, Al and individual Cu-Al IMCs in an acidic

chloride medium has been studied by employing a conventional three-electrode electrochemical cell. This is to mimic the conditions in devices encapsulated in epoxy mold compounds. Based on the electrochemical test results, palladium helps to improve the corrosion resistance of Cu and Cu-Al IMCs to chloride attack. The results imply that Pd-Cu wire should perform better than bare Cu wire in molded humidity reliability tests at the initial stage and after prolonged test durations. More studies such as industrial humidity reliability tests have to be conducted in the future to compare the effect of palladium distribution on the reliability of the Pd-Cu bonds in humid test conditions.

Based on the corrosion currents, Cu_9Al_4 is the IMC that is most prone to corrosion by acidic chloride solution. From literature, CuAl_2 IMC particles are formed in the as-bonded state between Cu and Al. At 24h of thermal annealing, Cu_9Al_4 is formed between the initial CuAl_2 and Cu. At long annealing durations, CuAl_2 and Cu_9Al_4 grow simultaneously and CuAl_2 is the main IMC until the Al pad is depleted where all CuAl_2 is converted to Cu_9Al_4 due to excess supply of Cu. Hence a thicker Al bond pad should be used to limit the amount of Cu_9Al_4 formed so as to reduce the failure rate of the devices in humidity reliability tests.

The test results show that in general, Pd helps to improve the corrosion resistance of the Cu-Al IMCs. Hence, the presence of a Pd layer at the bond interface and in the Cu_9Al_4 IMC layer could help to reduce the failure rate of Pd-Cu bonds in humidity reliability tests at longer test durations where the more corrosion prone Cu_9Al_4 is formed. TEM-EDX studies also show that Pd is present in the Cu_9Al_4 IMC layer (Figure 8.1) for Pd-Cu bond with Pd at the bond interface in the as-bonded state. Hence, it is necessary for Pd to be present at the bond interface in the as-bonded state for enhanced corrosion resistance.

Based on the results from this project, it is recommended to use low EFO current for Pd-Cu wire bonding. This is to produce a Pd rich layer at the bond interface. The Pd rich layer helps to improve the corrosion resistance of Cu and Cu-Al IMCs in humidity reliability tests due to attack by chloride in epoxy mold compounds. In addition, presence of Pd at the bond interface helps to slow down IMC growth between Cu wire bonds and Al metallization, resulting in less stress built up in the underlying pad layers for long term thermal reliability.

8.3 Recommendations for future work

Based on the understandings and conclusions from the current work, future scopes for additional in-depth works exist and are as follows:

1. With prolonged thermal annealing, cavities were observed in the Pd-Cu wire bonds with absence of Pd at the bond interface in the as-bonded state. It is postulated that the cavities could be due to the migration of Pd towards the bond interface during annealing. This explanation can be further substantiated by tracing the migration of Pd during thermal annealing through an in-situ heated TEM workholder. EDX line scans/mappings can then be performed at various annealing durations to analyze the correlation between Pd presence and cavities in the wire bonds.
2. From this project, it was observed that IMC particles were formed after initial stage of annealing and EDX line scan shows that Pd is not present in the initial IMC particles formed. After 24 h of annealing, two layers of IMCs are formed and Pd is present in the Cu rich IMC but not in the Al rich IMC. More TEM work has to be performed using an in-situ heated workholder to trace the diffusion of Pd through the bond interface and to explain why Pd is present in the Cu rich IMC but not in the Al rich IMC. High resolution transmission electron microscopy (HRTEM) can be performed to analyze the lattice structure and to observe if Pd stay inside the Cu-Al IMC lattice structure or it is segregated.
3. The effect of Pd on the type of IMC formed is not studied in this project. More work can be done to investigate if Pd affects the type of Cu-Al IMCs formed. If there is presence of Pd in one of the IMC layers, diffraction patterns can be obtained to check if it is similar to that without Pd.
4. It will be useful to investigate the IMC nucleation and growth process using in-situ TEM observation with a heated workholder. From the observations, we can study how Cu and Al inter-diffuse across a thin layer of native aluminum oxide at the initial stage of formation.
5. Mechanical and electrical tests can be performed with the annealed samples in order to establish a relationship between interfacial evolutions and interconnect properties. Based on the obtained results, the failure mechanism can be further explained.

6. It was reported in literature that properties of the epoxy mold compound such as chloride concentrations and pH levels has some effect on the reliability performance of copper wire bonds. Different chloride concentrations and pH levels of the corrosion medium can be used to test the corrosion performance of the samples in the electrochemical test. The corrosion current and electrical impedance of the samples can be measured. From there, a more detailed corrosion mechanism can be postulated. This test also allows us to identify the most significant factor (Chloride concentration or pH level) affecting the corrosion rate of Cu-Al IMCs.
7. In this research project, it was postulated that it is necessary for Pd to be present at the bond interface to improve the reliability of Pd-Cu wire bonds in humid conditions. Industrial reliability tests such as the highly accelerated temperature and humidity stress test (HAST) and pressure cooker test (PCT) can be conducted on Pd-Cu wire bonds with different Pd distributions, with bare Cu bonds as a baseline. The resistivity of the wire bonds at different durations can be measured. The results can be correlated and compared with findings from the electrochemical test.
8. In this research project, it was observed that presence of Pd at the bond interface helps to slow down the growth of excessive Cu-Al IMCs that might be detrimental to long term thermal bond reliability. Actual industrial tests with different types of external loadings and corrosion conditions could be performed on the devices, with the obtained results correlated to the growth of the IMCs.
9. Most of the current literature is focused on the first bond, i.e. ball bond, while there were few reports on the second bond, i.e. stitch bond although it plays an equally important role in determining the reliability of the bonds. A robust stitch response is critical. Currently there is lack of detailed knowledge on Pd-Cu stitch bonds; therefore an extensive investigation on such types of bond in the near future will be very relevant. Cross-sections of the stitch bonds can be done to study the IMC formation and growth rates with thermal annealing. The results can be correlated to the stitch bond response such as the pull strength and stitch lifts etc.
10. Bonded ball hardness can vary across the ball diameter. Ultrasonic vibrations assists in moving dislocations, vertical mechanical force applied via the capillary and transverse shearing motion of the capillary results in plastic deformations of the ball.

- Capillary geometry affects the force vectors acting on the FAB and compression of ball bonds. Finite element simulation of Pd-Cu bonded ball with different Pd distributions can be performed to show the stress variation across the ball diameter.
11. In this study, it was postulated that a thicker Al metallization helps to limit the conversion of CuAl_2 into the more corrosive Cu_9Al_4 IMC. This hypothesis can be further substantiated by studying the effect of Al pad thickness on Cu_9Al_4 growth rate at different annealing durations until the bond pad is depleted.

APPENDIX

Table A.1 EDX composition analysis of Cu alloys (wt.%)

Alloy	Element	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Average	Ideal	Stdev
Pure Cu	Cu	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0
Cu-1%Pd	Cu	98.8	98.8	98.8	98.9	98.8	98.9	98.8	99.0	0.0
	Pd	1.3	1.2	1.2	1.1	1.2	1.2	1.2	1.0	0.1
Cu-3%Pd	Cu	96.9	96.8	96.8	96.9	96.9	96.8	96.9	97.0	0.1
	Pd	3.1	3.2	3.2	3.1	3.1	3.2	3.1	3.0	0.1
Cu-10%Pd	Cu	90.3	90.1	90.1	90.1	89.9	90.0	90.1	90.0	0.0
	Pd	9.7	9.9	9.9	9.9	10.1	10.1	9.9	10.1	0.0

Table A.2 EDX composition analysis of Cu₉Al₄ alloys (wt.%)

Alloy	Element	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Average	Ideal	Stdev
Cu ₉ Al ₄	Cu	85.6	85.6	85.5	85.6	85.5	85.6	85.6	84.1	0.1
	Al	14.4	14.4	14.6	14.4	14.5	14.5	14.5	15.9	0.1
(Cu-1%Pd) ₉ Al ₄	Cu	85.7	85.5	85.2	85.1	85.1	85.2	85.3	83.2	0.2
	Al	13.5	13.7	14.0	14.1	14.1	14	13.9	15.9	0.2
	Pd	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.0
(Cu-3%Pd) ₉ Al ₄	Cu	82.7	82.7	83.0	83.0	82.8	83.0	82.9	81.6	0.1
	Al	14.3	14.3	14.0	14.1	14.2	14.1	14.1	15.9	0.1
	Pd	3.0	3.0	3.1	3.0	3.0	3.0	3.0	2.5	0.1
(Cu-10%Pd) ₉ Al ₄	Cu	77.1	77.2	77.0	76.9	77.1	77.0	77.0	75.7	0.1
	Al	14.3	14.2	14.4	14.4	14.3	14.3	14.3	15.9	0.1
	Pd	8.6	8.6	8.7	8.7	8.6	8.6	8.6	8.4	0.0

Table A.3 EDX composition analysis of CuAl alloys (wt.%)

Alloy	Element	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Average	Ideal	Stdev
CuAl	Cu	72.9	73.4	72.8	67.8	70.8	68.1	71.0	70.2	0.5
	Al	27.1	26.6	27.2	32.2	29.2	31.9	29.1	29.8	0.5
(Cu-1%Pd)Al	Cu	72.5	72.6	69.3	71.8	71.9	69.6	71.3	69.5	1.5
	Al	26.2	25.8	29.6	27.1	26.6	28.0	27.2	29.8	1.8
	Pd	1.3	1.6	1.1	1.1	1.5	2.5	1.5	0.7	0.6
(Cu-3%Pd)Al	Cu	68.6	68.2	70.8	69.6	69.2	71.1	69.6	68.1	1.0
	Al	27.0	27.7	27.6	28.5	27.4	27.4	27.6	29.8	1.6
	Pd	4.4	4.2	1.6	1.9	3.4	1.4	2.8	2.1	0.5
(Cu-10%Pd)Al	Cu	68.1	64.2	66.8	65.0	67.8	66.7	66.4	63.2	2.3
	Al	27.4	27.1	29.4	27.0	26.8	27.9	27.6	29.8	1.6
	Pd	4.5	8.7	3.8	8.0	5.4	5.4	6.0	7.0	0.7

Table A.4 EDX composition analysis of CuAl₂ alloys (wt.%)

Alloy	Element	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Average	Ideal	Stdev
CuAl ₂	Cu	56.2	55.2	55.8	56.6	56.8	56.8	56.2	54.1	1.5
	Al	43.8	44.9	44.2	43.4	43.2	43.2	43.8	45.9	1.5
(Cu-1%Pd)Al ₂	Cu	54.7	52.7	54.8	51.4	53.1	54.3	53.5	53.5	0.0
	Al	44.3	46.2	44.3	47.0	45.7	44.6	45.3	45.9	0.4
	Pd	1.1	1.2	1.0	1.6	1.3	1.1	1.2	0.5	0.5
(Cu-3%Pd)Al ₂	Cu	54.7	54.3	54.4	54.7	54.5	54.3	54.5	52.5	1.4
	Al	44.1	44.4	44.0	44.2	44.3	44.1	44.2	45.9	1.2
	Pd	1.2	1.4	1.5	1.1	1.3	1.6	1.3	1.6	0.2
(Cu-10%Pd)Al ₂	Cu	53.8	54.8	52.2	53.4	52.6	43.9	51.8	48.7	2.2
	Al	41.6	42.9	43.3	44.3	42.2	48.9	43.9	45.9	1.4
	Pd	4.6	2.3	4.5	2.4	5.2	7.2	4.3	5.4	0.8

Figure A.1 Backscattered image showing points for compositional analysis of Cu alloy

Figure A.2 Elemental mapping of cross-sectioned (Cu-10%Pd)Al₂ sample (a) Backscattered electron image and EDX mappings of (b) Cu, (c) Al and (d) Pd