Investigation of nano-copper for electronic packaging application : solder metallization and die attach

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2016

Luo, K. (2016). Investigation of nano-copper for electronic packaging application : solder metallization and die attach. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/66939>

<https://doi.org/10.32657/10356/66939>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**INVESTIGATION OF NANO-COPPER FOR ELECTRONIC
PACKAGING APPLICATION: SOLDER
METALLIZATION AND DIE ATTACH**

MASTER THESIS

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School of Materials Science and Engineering

2015

**Investigation of Nano-copper for Electronic Packaging
Application: Solder Metallization and Die Attach**

School of Materials Science and Engineering

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

2015

Abstract

Nano-copper (NC) has been developed recently with good potential for electronic packaging applications. In this work, the interfacial reaction between NC and Sn-3.5Ag and the adhesion between NC and different metallizations were investigated. Thermal Gravimetric Analysis (TGA) results of NC paste were used to help determine the best sintering condition of NC paste. Heating NC paste at 230 °C for 10 min at N₂ atmosphere is the optimal sintering condition. The sintered NC paste shows a porous nanocrystal structure.

In the solder interfacial reaction study with Sn-3.5Ag, plated Cu was used as a reference. Both sintered NC/Sn-3.5Ag and plated Cu/Sn-3.5Ag samples were reflowed for different time spans to obtain their morphology and kinetic information. The morphology changes from 10s to 5 hours reflow showed that the interfacial reaction of NC/Sn-3.5Ag is quite different from Cu/Sn-3.5Ag. NC/Sn-3.5Ag produces porous and elongated scallop-type Intermetallic Compounds (IMCs) while Cu/Sn-3.5Ag only forms scallop-type IMCs. The cause of this morphology difference is due to nano-copper's unique porous structure. Based on the Scanning Electron Microscope (SEM) and (Energy Dispersive X-ray Spectroscopy) EDS analysis of samples of different reflow times, an IMC growth mechanism in NC/Sn-3.5Ag has been proposed.

To quantify NC/Sn-3.5Ag and Cu/Sn-3.5Ag interfacial reaction, a kinetics analysis of the interfacial IMC growth was carried out. Results show that NC/Sn-3.5Ag reaction is faster than Cu/Sn-3.5Ag reaction. The growth of Cu₆Sn₅ in Cu/Sn-3.5Ag follows $t^{1/3}$ growth kinetics while the growth of Cu₆Sn₅ in NC/Sn-3.5Ag follows $t^{1/2}$ growth kinetics. By comparing experiment result with kinetics model, we conclude that the IMC growth in Cu/Sn-3.5Ag is controlled by diffusion through fast diffusion channel such as the IMC grooves while NC/Sn-3.5Ag reaction is mainly controlled by diffusion through the existing IMC layers.

In the adhesion study between NC and different metallizations, NC as a potential joining material was evaluated by cross-cut test and die-shear test. Different metallizations were prepared by either sputtering or electrochemical method. These metallizations are chosen because they are either commercialized in the industry or have shown very good

performance in lead-free solder applications. Even though NC can directly bond with Cu surface without forming IMCs, for the purpose of its potential as a joining material used in the future, it is essential to understand its adhesion conditions with different metallizations.

Different metallizations were prepared and analyzed by SEM, EDS and Atomic Force Microscope (AFM). The surface roughness, element concentration and metallization layer thickness were obtained and analyzed. Cross-cut adhesion test shows that Cu, ENIG, Cr/Ni/Au and Ni-Sn-P have relatively better adhesion with NC than Ni-P, Ni-W-P, Ni-Co-P. Shear test result reveals that Cu has the best adhesion with NC. By fractographic analysis of the shear test result, NC/Cu failure mode is verified as bulk (cohesive) failure, which resulted in higher failure strength. The failure mode of Ni-Sn-P/NC is bulk-partial IMC failure. The failure mode of Cr/Ni/Au and ENIG is bulk-partial pad peeling failure.

In summary, the morphology and kinetics study of NC/Sn-3.5Ag interfacial reaction have been carried out. The obtained information could be used as a reference in electronic packaging applications involving NC and Sn-based solders. Besides, the adhesion study between NC and different metallizations examines the potential of NC paste as a die-attach joining material. Experiment result shows that pure Cu has the best adhesion with NC after reflow at 230 °C for 10 min.

Acknowledgements

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

First of all, I sincerely express my great gratitude to my supervisor, Prof. Chen Zhong, for his invaluable guidance, advice, and encouragement throughout the course of this study. I would also like to thank my co-supervisor A/P Gan Chee Chip. Without his supervision and constant support, this work could not be possible.

Next, I thank Dr. Lee Byunghoon for his sincerely advice and guidance all the time. I would also like to thank my colleagues in NC group: Zhenggang, Meizhen, Jaewon, Huiteng, and Yuanyuan for their friendship and sound advice. I am also thankful to colleagues in Prof. Chen and A/P Gan's group, for their help and kindness.

I am thankful to all of my friends in the school of Materials Science and Engineering, Nanyang Technological University, for their inspiration. I am also thankful to Dr. Li Yi (CityU) and Dr. Lee Byunghoon for reviewing my thesis and invaluable suggestions. I am also thankful to my friend Li Wenjie and Chang Lei for their research assistance. I appreciate the help from technical staffs: Ms. Yeow Swee Kuan, Mr. Lim Yan Koon, Mr. Lim Ming Pin, Alan, Dr. Ang Derrick, Dr. Zviad Tsakadze and Mr. Tan Jok Boon.

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

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Abbreviations

NC	Nano-copper
TGA	Thermal Gravimetric Analysis
DIP	Dual-in-Line
IMCs	Intermetallic Compounds
IC	Integrated Circuit
I/O	Input/Output
VLSI	Very Large Scale Integration
PGA	Pin Grid Array
SOP	Small Out-Package
QFP	Quad Flat Package
BGA	Ball Grid Array
CSP	Chip Size Package
UBM	Under Bump Metallization
TSM	Topside Metallurgy
TSV	Through Silicon Via
ENIG	Electroless Nickel Immersion Gold
EN	Electroless Nickel
CVD	Chemical Vapor Deposition
PVD	Physical Vapor Deposition
MBE	Molecular Beam Epitaxy
EU RoHS	European Restriction of Hazardous Substances
SAC	Sn-Ag-Cu
CCVC	Combustion Chemical Vapor Condensation
SEM	Scanning Electron Microscope
EDS	Energy Dispersive X-ray Spectroscopy
BSI	Back-scattering Image
AFM	Atomic Force Microscope

Chapter 1 Introduction

1.1 Background and Motivation

Electronic industry has been booming over the past 40 years and the trend is continuing. Nowadays, the electronic device becomes more functional and smaller than before. The development of electronic device has largely changed people's everyday life. In fact, the achievements in electronic industry rely on several breakthroughs in electronic packaging. From generation to generation, electronic packaging evolves from the first DIP (Dual-in-Line) packaging to today's flip-chip technology or 3D packaging.

In electronic packaging development roadmap, several challenges exist, for example, the presence of toxic material in solder, higher I/O (Input/Output) counts requirement, heat dissipation problem and reliability issue. In the past, eutectic Pb-Sn solder was used due to its good soldering performance. However, Pb is a mildly toxic metal both towards human body and the environment. Therefore, Pb-based solders are replaced by lead-free solders. Besides, with better design and new packaging methods, I/O counts become higher without heat dissipation problem. The reliability problem, especially the fast growth of Intermetallic Compounds (IMCs) has been topic of research for decades.

Up to now, there are still issues with the commercially available Sn-based lead-free solders, such as fast IMCs growth, Sn whisker formation etc. An alternative joining material, Ag paste consisting of micro- or nano-sized particles, has been explored in recent years [20, 26]. The joint formed by Ag paste has better thermal and electrical conductivity than traditional Sn-based solders. And this paste can be soldered at a low temperature similar to Sn-Pb solder, and applied in a higher temperature environment due to the high melting point of Ag. However, Ag has an ion migration problem under high temperature and humidity conditions and the production cost is high.

A new solder material, nano-copper (NC), was recently developed [36]. NC shares the advantages of Ag paste, while has relatively cheaper price. The NC paste is composed of three parts: NC particles, organic capping layer and solvents. The NC particles are the main joint material upon fusion. Organic capping layer prevents NC from oxidation, and the solvents provide viscosity of the paste. After sintering, NC shows a porous nano-crystal structure; sometimes cracks may exist due to the loss of the organic solvent. For

the purpose of investigating NC's potential for electronic packaging application, NC as a metallization and NC as a die attach (joining) material have been studied in this thesis.

1.2 Objectives

1.2.1 Morphology and kinetics study of interfacial reaction between NC and Sn-3.5Ag

In this part, NC was used to form a metallization first. The differences between NC and plated Cu in their interfacial reaction with lead-free solder are studied. The objective is to understand the morphology, reaction kinetics, and intermetallic growth mechanism of NC with Sn-based lead-free solder.

1.2.2 Adhesion study between NC and different metallizations

This part focuses on NC joining applications. The adhesion between NC and different metallizations (Cu, Cr/Ni/Au, ENIG, EN, Ni-Sn-P, Ni-W-P and Ni-Co-P) are studied. The purpose is to evaluate adhesion strength between NC and silicon substrate, as well as to understand the joining failure mechanisms.

Chapter 2 Literature Review

Introduction

NC paste was recently developed with the potential of forming a metalized layer or being used as an alternative soldering material. The present work investigates NC as a potential solder metallization and die attach material. This chapter reviews the literature on electronic packaging, silver paste, NC paste and Cu-Sn IMC formation based on the phase diagram.

2.1 Electronic Packaging

Simply speaking, electronic packaging is an engineering method to connect electronic parts together both mechanically and electrically and to protect the electronic chips or components from damaging. Packaging plays an indispensable role in electronic devices design and manufacture. A suitable packaging method can largely decrease the production cost of electronic devices as well as provide good quality of the final product. Electronic packaging is usually classified into three levels. The first level packaging is to connect integrated circuits in a silicon chip to its substrate in order to provide basic functions, such as interconnecting, protecting, cooling and powering. The next step is to package the first level parts to a board, which is the second level packaging. The third level packaging is to place the board to backplane. The packaged electronic system will be encapsulated in the backplane so as to finish the final step of packaging. Figure 2.1 illustrates the packaging hierarchy.

2.1.1 Electronic Packaging Category and History

Electronic devices evolve very fast over the recent 30 years. For example, today's cellphone is much smaller and carries more functions than before. Technically, in integrated circuits industry, this trend is called the Moore's Law. Moore's Law predicts that the number of transistors in a dense integrated circuits doubles approximately every two years[1]. The development of ICs also promotes electronic packaging technique to

progress. Electronic packaging method, from the earliest ceramic flat packs to nowadays popularized flip-chip, has already made great achievement[2].

The first commercialized circuit packaging is DIP (dual in-line package). Its rectangular packaging box has two parallel rows of pins on both sides, as shown in Figure 2.2 (a). This packaging format was invented by Don Forbes, Rex Rice and Bryant Rogers at Fairchild R&D in 1964[2].

Figure 2.1 Packaging hierarchy[3]

However, as the integration of the integrated circuits keeps growing and the pin counts of DIP could not meet the need of VLSI (very large scale integration), another through-hole packaging, PGA (pin grid array) appeared in 1980s. PGA arranges its pins on the underside of the square package so as to increase pin counts as shown in Figure 2.2(b).

Figure 2.2 Through-hole package and surface mount package[3]

Besides the through-hole packages, another category of IC packaging is surface mount, which came into being in the early 1980s and became popular in the late 1980s. SOP (small out-package) is a good example of surface mount packaging, which was very popular in I/O (input and output) memory application because of its low cost. QFP or CFP (Quad flat package) is an extension of SOP. The quad package has “gull wing” leads extending from each of the four sides[4]. Also, there are some other types of surface mount package, such as Leadless Chip Carrier (LCC) and Plastic Leaded Chip Carrier (PLCC). But they have limited applications. At the end of 1980s, solder balls were introduced as an alternative choice for packaging connection, as solder balls can be put beneath the package to form die attachment which significantly increases the I/O count of the package. BGA (Ball grid array) is an example of this technique.

In order to fulfill the requirement of modern electronics packaging, that is, thinner, smaller and lighter, CSP (chip size package) was introduced. Flip chip technology is a kind of CSPs. Due to its several advantages, such as much higher I/O count, higher signal

propagation performance and easier for one step manufacturing, flip chip predominated nowadays the IC packaging industry[3, 5, 6]. An illustration of flip chip is shown in Figure 2.3.

Figure 2.3 General configuration of Flip chip[6]

Flip chip packaging contains a specific metallization. The chip side metallization is called UBM (Under Bump Metallization) and the substrate side metallization is called TSM (Topside Metallurgy). For the purpose of better adhesion and decrease packaging's early fatigue failure, under-fill material is filled in the gap[3].

In order to make more dense ICs, three dimensions packaging was proposed. At first, two or more chips were stacked vertically together by wire connection. As it requires extra “interposer” between different layers, another design, TSV (through silicon via) gradually replaced this wire connection. In TSV, stacked chips are interconnected together by allowing several vertical electrical via passing through them[7]. A schematic illustration of TSV structure is shown in Figure 2.4.

Figure 2.4 Schematic illustration of 3D semiconductor with TSV (Through Silicon Via) technology[8]

In summary, it has been observed that electronic packaging evolves very fast over the past 30 years. This evolution is shown from the package roadmap in Figure 2.5. From the first generation of commercial packaging, DIP, to the latest TSV technology, packaging has made electronic devices much denser, lighter, and more powerful. With the help of many smart electronic devices, our daily life becomes more and more convenient. To enable future development of electronic devices, further study of new electronic packaging technology and materials is of great importance.

Panda Europe - June '98

Figure 2.5 Package Roadmap[9]

2.1.2 Packaging Metallization

Metallization is a very important part in electronic packaging. For example, in flip chip technology, a good metallization is able to improve its packaging reliability. Although there are many different kinds of metallizations in packaging, generally, the metallization consists of three major layers: adhesion layer, wetting layer and oxidation barrier layer. The function of the adhesion layer is to form a strong bond to the substrate. The wetting layer should remain intact in some extent during the reflow process. The oxidation barrier layer is to protect the wetting and adhesion layers from oxidation[5, 10].

In the past, IBM's ball-limiting metallurgy structure uses Cr/Cu as the adhesion layer, Cu as the wetting layer and Au as the oxidation barrier layer[5]. However, considering its cost for mass production as well as metallization quality, ENIG (electroless nickel immersion gold) is adopted as an alternative metallization scheme.

There are several kinds of methods to form the electronic packaging metallization layers. They include vapor deposition, chemical and electrochemical methods, and roll-to-roll coating. Vapor deposition comprises CVD (chemical vapor deposition) and PVD (physical vapor deposition). CVD, such as molecular beam epitaxy (MBE) is used for single crystal deposition in semiconductor industry. In physical vapor deposition, high vacuum condition is required and sometimes magnetron or electron beam is also applied. Some high quality thin film metallization, which has nanometer size thickness, is usually deposited by vapor deposition.

Chemical and electrochemical methods include electroplating, and electroless plating. Electroplating uses electrical current to reduce metallic cations to form a coherent metal coating on an electrode. Current density of electroplating is the key parameter to determine the metallization thickness. Electroless plating is a common method to form nickel-phosphorus (Ni-P) alloy. Reducing agent, for example $\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$, reacts with nickel ions to deposit a layer of Ni-P on the substrate. In general, the thickness of metallization formed by chemical and electrochemical methods is around 1 to 100 micrometer.

Roll-to-roll coating process is a method to form a thick metallization. Meyer bar coating or screen-printing is usually used to coat solder paste in the packaging. Even though the metallization formed by this method may not be really flat, this method is widely applied due to its convenience and low cost. Actually, stencil printing or bar coating with the combination of mass reflow process has already been widely used in soldering process. Some other metallization formation methods such as inkjet printing, lithography and spin coating are also utilized for some new materials.

2.1.3 Packaging Joining Methods

In order to interconnect different chips or electronic devices with the substrate, different ways of joining can be applied. Metallic wires, solders, conductive adhesives are three major joining materials.

Wire bonding uses metallic wire as interconnections in IC or other semiconductor device fabrication. Four major metals, that is, copper, gold, silver and aluminum, are used in wire bonding. Good thermal and electrical conductivity of copper as well as its comparable low cost makes copper the most favored material in wire bonding packaging[11]. Due to different connection process, wire bonding is classified into three major classes: ball bonding, wedge bonding and compliant bonding[12]. No matter what kind of wire bonding it is, the process could be summarized as attaching two ends of the wire with the combination of heat, pressure or ultrasonic energy.

Another main method of joining is soldering, which is a way to join two or more metal components together at a low temperature (150-300 °C). Solder paste is often used in soldering. It consists of flux, printing vehicle and metal powder. A typical constitution of solder paste is shown in Figure 2.6.

Figure 2.6 Typical constitution of solder paste [13]

The metal powders used in solder are tin, lead, silver, zinc, aluminum and their alloys. Eutectic alloys are usually used because partial melting can be prevented by the single and low melting point of the eutectic alloy. In the past, lead-tin solders were extensively utilized because of its comparable low melting point, narrow temperature gap of melting

and control of tin whisker[14]. However, lead is a mildly toxic metal both towards human body and the environment. Considering its toxicity, international legislation from EU RoHS (European Restriction of Hazardous Substances) has prohibited the use of lead in manufacturing consumer electronic products since July 2006[15]. Instead, lead-free solders are used to replace the eutectic lead-tin solders. There are many different kinds of lead-free solders. Sn-Ag, Sn-Bi, Sn-In, Sn-Zn and especially SAC (Sn-Ag-Cu) are commercialized lead-free solders [16]. The flux and print vehicle gives solder cream its “pasty” nature. These components keep the solder powder evenly dispersed throughout the paste and also prevent particles from precipitating. Besides, in soldering, the flux is able to remove rust and prevent further rust. In real application, solder has a variety of forms, such as, paste, powder or ball, wire and bar. The choice depends on the soldering process and specific applications.

Conductive adhesives are sticky glues that hold two electronic components together. These adhesives are very commonly used for attaching dies to the substrate. Besides, they are also used in laminated printed circuits. Conductive adhesives are made by a combination of a sticky component and conductive particles. Conductive particles, such as silver, copper or graphite or some eutectic alloys are suspended in the sticky paste. The sticky paste is usually made of one or more varnish or resin. Silver particle is one of the most popular filler materials in conductive adhesives. More details of silver pastes will be discussed later.

There are some differences between solders and conductive adhesives. Solders form a metallurgical joint while conductive adhesives form a mechanical and chemical bond. This difference leads to different performance in electrical packaging. First of all, solder joint has better electrical conductivity than adhesives. The thermal conductivity in solder is higher than adhesives and volume resistivity for solder is less than adhesives. Besides, in their applications, solders can only be used for solderable materials while conductive adhesives can be used for non-solderable substrate. Actually, conductive adhesives are the only joining option for non-solderable substrate. Furthermore, another difference is solder joint can be re-soldered, but conductive adhesives cannot be reworked easily.

All in all, there are three major packaging joining methods: metallic wires, solders and conductive adhesives. They form different joints in various packaging situations. In reality, sometimes a package uses a combination of these three joining methods.

2.2 Silver Paste

In 2.1.3 Packaging joining methods, silver paste is mentioned as a conductive adhesive in die-attach joint. This paste consists of suspended silver particles and sticky component. Different from traditional conductive adhesives, today's silver paste can also form metallurgical joint by decomposing organic part through sintering. One important character of this silver paste is that the size of the metal particles inside the paste will influence the sintering temperature of the paste. In the consideration of this character, the silver paste is introduced at both micro- and nano-scale.

2.2.1 Micro-scale Silver Paste

Micro-scale silver paste means the silver particles used in the paste is micrometer size. The early work of silver paste is led by Schwarzbauer and his team [17]. In order to decompose the solvent, a step of preheating was utilized. At low temperature (around 200 °C), the micro-scale silver paste will only form a very porous Ag joint. Given this condition, a pressure around 9 MPa was applied in this micro-scale silver paste sintering[17]. This pressure was used because it increases the sintering driving force and thus helps [18] eliminate fraction of pores. As a result, the porous silver joint will be densified through the pressure sintering[19].

Besides the micro-silver itself, another main component is the solvent or paste. The composition of this part varies a lot. Different patents holds different solvent composition, such as cyclohexanol[17, 20], butanol[21], terpineol[22] and cyclohexanol–methanol[23]. No matter what kind of solvent is applied, the aim of the solvent is to decompose once the die-attachment is formed. Micro-scale silver paste has some advantages, such as low thermal stress with the substrate, good heat dissipation, good long-term thermal and electrical contact between die and substrate. It is these advantages that make micro-scale silver paste widely used in some electronic packages.

2.2.2 Nano-scale Silver Paste

Due to the relatively large size of particles inside the micro-scale paste, the sintering process is not very convenient to implement. Besides adding pressure in the sintering process, decreasing the silver particle size is also an option to fulfill a more densified silver joint. As it is well known, nano-scale particles tend to agglomerate because of their high surface energy [24], and this character helps nano-scale silver particles to be sintered at relatively lower temperature while having a comparable densified structure.

The history of nano-scale silver paste traces back to 1969 when Frens and Overbeek synthesized colloidal silver[18]following the approach developed by Carey Leain 1889. Since then, several researches have been done in nano-scale silver paste [17, 20-23, 25, 26]. Generally speaking, there are two major methods of synthesizing nano-scale silver paste. The first way is through precipitation. The nano-scale silver paste is made by reducing or precipitating silver nanoparticles from silver salt. Several reducing agents are utilized in this process, such as ascorbic acid[27], sodium citrate[28], or sodium citrate dihydrate[29]. Another method is combustion chemical vapor condensation (CCVC). Silver nanoparticles are produced by combusting Ag-bearing precursor in the oxygen stream[30].

The composition of nano-scale silver paste consists of three parts: organic capping layer, binder, and solvents[31]. As shown in Figure 2.7, the function of organic capping layer or dispersant is to provide steric resistance and protect Ag particles from melting or agglomeration. The function of binder is to prevent quick drying of silver paste during operation. The quick drying of silver paste may lead to cracks on the final product. The thinner or solvent is to ensure the viscosity of the paste so that it can be used in screen-printing or bar coating, which has been mentioned in 2.1.2 packaging metallization.

Figure 2.7 The formulation of nano-scale silver paste[31]

Nano-scale silver paste has many advantages. Though belonging to conductive adhesives, nano-scale silver paste is unlike traditional conductive adhesives. It forms pure silver joint instead of chemical or mechanical bonding. This pure silver joint has better thermal and electrical conductivity than the traditional one. Besides, the low temperature process of nano-scale silver paste gives it a potential application in flexible electronics [28, 29, 32, 33]. Furthermore, since silver has a melting point of 961 °C, the pure silver joint formed by nano-scale silver paste can serve in high temperature environment[34]. As it is mentioned in 2.1.3 packaging joining methods, lead-free material is required in today's electronic packaging. Nano-scale silver paste is also an option for lead-free packaging.

However, there are several unsolved disadvantages of nano-scale silver paste. First of all, silver has an ion migration problem under high temperature and humidity conditions. Ion migration creates vacancies or voids in the joint interface, which largely decrease joint reliability [10]. Besides, the expensive price of silver limits its massive popularization. Therefore, a more reliable and cheaper paste which keeping the advantages of nano-scale silver paste is needed.

2.3 Nano-copper (NC) Paste

In order to reduce the cost of nano-scale metallic paste, NC paste, which shares similar low melting point and good thermal and electrical conductivity as nano-scale silver paste while having much cheaper price ($1/100^{\text{th}}$ the cost of silver), has come into sight. During the past five years, several patents and papers about preparing NC have been published [35-37]. Generally speaking, these methods of preparing NC have two purposes to achieve. First, the obtained nanoparticles should be uniform and stable under ambient condition. Second, the procedure should not be very expensive and is able to achieve large-scale manufacturing.

Similar to nano-silver particles, NC particles also have a problem of oxidation and self-aggregation. In order to avoid this problem, protective layers around NC particles are utilized. These layers can be amphiphilic molecular or polymers, or other inert metal like silver, as it is shown in the Figure 2.8.

Figure 2.8 Protection and functionalization of copper nanoparticles with a shell (a) an organic surfactant and (b) a metal and an organic surfactant [38]

Synthesis of copper nanoparticles is mainly divided into two categories: metal demolition process and salt reduction process. Metal demolition process means bulk metal substrates are demolished down to nanometer scale particles through various

physical methods. While salt reduction process means metal nanoparticles are reduced from metal derivatives through different process.

Considering different wet chemistry, salt reduction process can also be divided into two types: biphasic procedure by applying reverse micelles and single phase procedure by using polar organic solvents. Reverse micelles procedure has advantage in size control of nanoparticles[39]. For example, Zinn and Lu produced small and narrowly distributed NC paste by using complexing amines[36]. For single phase procedure, the most representative one is polyol method. For example, Yan and Zhou's use PVP as a protective agent and different polyol as the reaction medium[35].

As for its application, NC paste can be used in catalysis[40], lubrication[41], antimicrobial agents[42, 43] and electronics. In electronics, paste form NC can be combined with stencil print and mass reflow to replace commercial lead-free solder in the future. Ink form NC could be processed by ink-jet printing or spinning coating to form a thin layer of conductive copper[44]. This method can form a conductive copper layer on flexible substrate, which may replace silicon based electronic devices in the future.

In NC processing, sintering is always required. Sintering can remove organic part of the NC paste and form a porous layer. The formation of porous NC is classified as a template method in fabricating nanoporous metals [45]. The FIB-polished NC sample is shown in Figure 2.9. The porous structure gives sintered NC better failure resistance, though its fatigue failure is brittle type like IMC (Intermetallic) failure [46]. In the future, more investigation is needed for the properties of porous NC and other porous metals [45]. These properties will be a good reliability reference for its future application.

Figure 2.9 FIB-polished NC Sample Showing porosity after 168 h at 150 °C [46]

In summary, NC is a promising material for electronic packaging applications. Several patents and papers about its preparation have been published. Considering its good thermal and electrical conductivity and relatively cheap price, NC could be one of the most promising candidates to replace lead-free solders or to be used as a new metallization material. Different from other materials, NC will form a porous structure once sintered at certain temperature, which holds a quite different character than dense copper made by conventional methods. Even though several studies about copper have been done before, properties about porous NC is still unknown such as its reaction with Sn-based solders when used as a metallization layer. Therefore, for its future applications, it is essential to study properties of this porous NC during solder reaction, as well as adhesion when used as a joining material.

2.4 Cu-Sn Phase Diagram

In electronic packaging, IMCs (Intermetallic compounds) are a key component for the packaging reliability. The growth of IMCs will lead to brittle fracture in the solder joint, which will largely decrease the electronic device's service life [47]. Therefore, it is necessary to study IMCs. Among all the IMCs, Cu and Sn IMCs are most widely encountered in the electronic packaging. Some basic understanding of their reaction and their phase diagram is necessary. In the Cu-Sn system, several different IMCs, such as Cu_3Sn (ϵ), Cu_6Sn_5 (η), Cu_6Sn_5 (η'), $\text{Cu}_{10}\text{Sn}_3$ (ζ) will form [48], as shown in the Figure

2.10. In the temperature range of interest (below 350 °C), Cu_3Sn (ϵ), Cu_6Sn_5 (η), Cu_6Sn_5 (η') are the IMCs formed in this system. Cu_6Sn_5 has two structure forms: stable form η' and metastable phase η . The stable form η' which has long-period super-lattice is formed at room temperature while the metastable phase η is formed at high temperature. The equilibrium transformation temperature between these two phases is 186 °C. The Cu_6Sn_5 (η) was first reported to be of the NiAs structure type (P63/mmc, $a=4.190$ Å and $c=5.086$ Å) by Westgren & Phragmen in 1928[49]. While Cu_6Sn_5 (η') was reported to be of the NiAs- Ni_2In superstructure [50]. The nominal composition of the two IMCs is shown in Table 2.1.

Figure 2.10 Cu–Sn binary phase diagram [45]

Table 2.1 Standard Cu and Sn percentage in Cu₆Sn₅ and Cu₃Sn

	Atomic%	Mass%
Cu₆Sn₅		
Cu	54.5	39.07
Sn	45.5	60.93
Cu₃Sn		
Cu	75	61.63
Sn	25	38.37

Chapter 3 Morphology and Kinetics Study of Interfacial Reaction between NC and Sn-3.5Ag

Introduction

The kinetics and morphology study of copper and Sn-3.5Ag has been investigated before [10, 14, 51-62]. However, little has been studied in NC and Sn-3.5Ag reaction. Through K. Schnabl et al.'s result [46], it is known that NC paste will form a porous structure after sintering. However, the porous NC and Sn-3.5Ag interfacial reaction hasn't been studied. In this Chapter, a detailed experiment of NC/Sn-3.5Ag interfacial reaction was carried out with electroplated dense Cu as a reference. The reaction mechanism, morphology, kinetics analysis of both NC/Sn-3.5Ag and Cu/Sn-3.5Ag were compared and explained.

3.1 Experimental Procedure

The experiment procedure is briefly introduced in Figure 3.1. Before NC was bar coated, a 2- μm Cu was sputtered on silicon substrate as an adhesion layer. After the NC was sintered, Sn-3.5Ag lead-free solder in paste form was applied and reflowed. The samples were then analyzed using SEM and XRD. For the reference samples, a thick layer (30 μm) of Cu was electroplated. More details are given later.

Figure 3.1 Illustration of the Experiment Procedure: cross-section sample and top view sample.

3.1.1 NC Preparation and Analysis

Before starting the experiment, processing-related properties of NC paste are studied. The NC paste, namely CuquantumFuse™ Paste, is invented and provided by Lockheed Martin Advanced Technology Center. This paste has also been studied in K. Schnabl et al. [46]. The raw CuquantumFuse™ Paste has to be washed before utilization. Then washed NC paste was tested by TGA (Thermal Gravimetric Analyzer) Q500 to obtain the decomposition temperature of its organic part. The ramping up speed of TGA is 3°C/min. The weight of the paste used in the TGA test is 19.742mg.

3.1.2 Preparation of Test Samples

After obtaining the TGA data of the NC paste, steps of preparing test samples followed. Several 6 inch silicon wafers were washed first following the AMI cleaning procedure [63] using acetone, methanol and isopropanol to remove debris or residues from the silicon wafer surface. Once the silicon wafer was cleaned, they were put into Kurt J Lesker PVD 75 (shown in Figure 3.2) to sputter a layer of 2 µm thick copper. Then these sputtered copper silicon wafers were cut into several 5*5 mm chips. By utilizing Meyer Bar-coating, NC paste was printed on the 5*5 mm sputtered copper chips. These printed chips were put into a home-made reflow oven (shown in Figure 3.3) and sintered at 230°C in N₂ atmosphere for 10 min. Sn-3.5Ag solder paste was then printed on the sintered NC chips with Meyer bars. This multiple layer structure is illustrated in Figure 3.4 (b). The sample preparation of Cu group is the same as NC group, except that copper group didn't have a layer of NC. The 30µm-thick Cu layer in Figure 3.4 (a) is coated by electro-plating.

Figure 3.2 Kurt J Lesker PVD 75

Figure 3.3 Home-made reflux oven.

After applying a layer of Sn-3.5Ag solder paste through screen-printing, the sample was put into Memmert UP 400 oven (As shown in Figure 3.5) to reflow at 230°C for different times. The Sn-3.5Ag solder and Cu or NC interfacial reaction is liquid-state reaction,

because at 230 °C, the Sn-3.5Ag solder has already melted (melting point of Sn-3.5Ag solder is 221 °C [14]). As solder paste has flux to protect sample from oxidation, the reflow process was carried out in ambient condition. The holding time was varied from 10 s, 30 s, 2 min, 5 min, 20 min, 40 min, 60 min, 1.5 h, 2.5 h to 5 h. The reflowed copper and NC samples are shown in Figure 3.6.

Figure 3.4 Schematic of sample metallization layout (a) NC (b) copper

Figure 3.5 Memmert UP 400

Figure 3.6 Reflowed samples (a) copper (b) NC.

3.1.3 Microstructure Observations

For microstructure observation, the prepared samples were divided into two groups: cross-section and top view.

The cross-section samples were cold mounted in epoxy and polished down to 1 μm finish. After polishing, solder etching was carried out with an etching solution (95wt% ethanol, 4wt% nitric acid, 1wt% hydrochloric acid). The polished samples were dipped into the etching solution for 5 min to dissolve the extra solder. N_2 gun was used to dry etched samples. After being dried by N_2 gun, specimens were coated with a thin layer of gold in order to prevent charging during SEM observations. The prepared cross-section observation sample is shown in Figure 3.7. JEOL JSM-6360A Scanning Electron Microscope (SEM) was used for microstructure analysis. EDS (Energy Dispersive X-ray Spectroscopy) was performed to analyze the chemical composition of the interfacial compounds.

Figure 3.7 The prepared cross-section sample.

For top-view sample, they were also cold mounted in epoxy. In order to reveal IMCs on the surface, solders was etched out with the same etching solution (95wt% ethanol, 4wt% nitric acid, 1wt% hydrochloric acid). The preparation of top-view sample is similar to cross-section sample. The prepared top-view sample is shown in Figure 3.8. SEM was applied to view the top-view morphology and X-ray Diffraction (XRD) was used to

identify the crystal structure of the IMCs. XRD studies were carried out at the Bruker D8 Advance. The XRD spectra were obtained in the 2-theta mode with 40 kV voltage, 40 mA current, 5 degree insert angle and the scan speed of 0.5s/step.

Figure 3.8 The prepared top-view sample

An image processing and analyzing software, Imagepro Plus, was utilized to measure the length, thickness of the IMCs (Intermetallic compounds) based on the SEM images taken. The thickness of interfacial IMCs was determined by dividing the measured IMC area with the length. The reported IMC thickness was an average of measurements at five different locations in the same sample.

3.2 Results

3.2.1 NC TGA Result and Optimal Reflow Process

The TGA result of QuantumFuseTM Paste is shown in Figure 3.9. Before 200 °C, there are two weight reduction peaks: 66.09°C and 167.37°C. They represent the decomposition of the organic additives in the NC paste. From 200°C to 230 °C, the cause of weight reduction is the decomposition of the capping layer surrounding NC particles. Through a series of experiment and related paper search, a standard sintering process has been obtained. The reflow curve of this sintering procedure is shown in Figure 3.10. The reflow is under N₂ atmosphere to prevent Cu oxidation. At first, the sample was put into the oven with around 10°C/ min ramping up speed. Once the temperature reached 230°C,

it was maintained at this temperature for 10 min for fully decomposing organic residues. After that, the sample was annealed with the chamber to 150°C and then cooled down to room temperature at a faster cooling rate.

Figure 3.9 TGA result of NC paste

Figure 3.10 NC paste reflow curve

3.2.2 Cu/Sn-3.5Ag IMC Morphology during Liquid-State Reaction

Cu/Sn-3.5Ag reaction has been widely studied, and it is found that scallop-type Cu_6Sn_5 will form during the liquid state Cu/Sn reaction [56, 64, 65]. And as the reflow continues, a thin layer of Cu_3Sn followed with voids will form between Cu and Cu_6Sn_5 . This fact can be proved in Figure 3.11, which shows the cross-sectional interfacial SEM image of Cu/Sn-3.5Ag. By combination with XRD data shown in Figure 3.12, the white scallop-type grains are verified as Cu_6Sn_5 . The thin grey layer is Cu_3Sn . Beneath the thin grey layer, a darker grey layer is sputtered Cu. The bottom dark layer is silicon substrate.

Figure 3.11 SEM BSI of Cu/Sn-3.5Ag interfacial reaction after reflow for 5 h at constant 230 °C.

As for evolvement or reaction mechanism between Cu and Sn, the recognized theory stated that the total volume of scallop-type Cu_6Sn_5 will become bigger and bigger driven by the formation energy of intermetallic compound. As the copper grains grow bigger, the channels providing Cu will become less and therefore, the growth of Cu_6Sn_5 will be reduced. However, in order to maintain the growth of Cu_6Sn_5 , the scallop will elongate [10]. The results shown in the Figure 3.13 reflects this evolvement. Each picture

represents different reflow times. From (a) to (j), they are 10 s, 30 s, 2 min, 5 min, 20 min, 40 min, 60 min, 1.5 h, 2.5 h and 5 h.

Figure 3.12 XRD pattern of Cu/Sn-3.5Ag interfacial reaction after reflow for 5 h at constant 230 °C

Figure 3.13 SEM BEI of Cu/Sn-3.5Ag interfacial reaction (a)-(j) represents the reflow time of 10 s, 30 s, 2 min, 5 min, 20 min, 40 min, 60 min, 1.5 h, 2.5 h and 5 h.

3.2.3 NC/Sn-3.5Ag Morphology during Liquid-State Reaction

Two types of analysis for the NC/Sn-3.5Ag liquid-state reaction are made: cross-section and top-view. The cross-section images are shown in Figure 3.14. Since backscattering image could provide a good composition contrast of different element[66], the Backscattering mode is utilized. From Figure 3.14, a gradual evolvement of the IMC is shown: from small scallop-type layer surrounding the NC to bigger and elongated scallop-type IMCs.

Figure 3.14 Cross-section SEM BSI of NC/Sn-3.5Ag; reflow time (a) 10 s, (b) 30 s, (c) 2 min, (d) 5 min, (e) 20 min, (f) 40 min, (g) 60 min, (h) 1.5 h, (i) 2.5 h, (j) 5 h.

The top-view images are shown in Figure 3.15. Since secondary electron will reflect better topographic information[66], the Secondary Electron Image (SEI) mode is used. From Figure 3.15 (a)-(h), IMCs started from small scallop-type grains to elongated IMCs and finally are densified to a dense porous IMCs. The result of Figure 3.15 corresponds to the result of Figure 3.14.

Figure 3.15 Top-view SEM BSI of NC/Sn-3.5Ag; reflow time (a) 30 s, (b) 2 min, (c) 5 min, (d) 20 min, (e) 40 min, (f) 60 min, (g) 1.5 h, (h) 5 h.

3.3 Discussion

3.3.1 The Phase Composition

From the cross-section image of the interfacial reaction between NC and Sn-3.5Ag, several different layers or compositions are detected. They are porous NC, Cu, Cu_6Sn_5 and porous Cu_6Sn_5 .

Figure 3.16 shows SEM BSI of NC/Sn-3.5Ag reaction with 1 min reflow time. In order to observe top view morphology as well as cross-section image, the sample was tilted in the SEM chamber. The marked (rectangular) regions were analyzed by EDS.

In Figure 3.16, square 007 demonstrates the plated Cu layer in the experiment. The EDS result of this region, which verifies the Cu composition, is shown in Figure 3.17.

Figure 3.16 SEM BSI of NC/Sn-3.5Ag interface after 1 min of reflow.

Element(KeV)	At%	Mass%
Cu K	100	100

Figure 3.17 EDS compositional results of Cu in Figure 3.12 007 region

A porous NC is present on top of the Cu layer, which is revealed in Fig 3.16 006 region. The EDS result of region 006 indicates 100% Cu as in region 007.

Porous Cu_6Sn_5 was formed first, and some dense Cu_6Sn_5 also forms after long time of reflow.

In square region 001 and 002, an obvious porous IMC layer is found. The EDS result of it is shown in Figure 3.18. The Cu at% is 52.24, which is close to Cu at% in Cu_6Sn_5 .

Besides, in Figure 3.15, the NC/Sn-3.5Ag reflow time from (a) to (h), these porous IMCs are also observed. In order to verify the exact phase of the IMC, X-Ray Diffraction (XRD) was utilized. The XRD pattern of NC/Sn-3.5Ag after reflow for 5 h at constant 230 °C is shown in Figure 3.19. Cu, Ag₃Sn and Cu₆Sn₅ are detected, and it implies that the X-ray has penetrated the IMC layer into NC layer. Besides, it also indicates that Sn-3.5Ag solder has been etched away.

No Cu₃Sn composition is detected in Figure 3.19, which means after 5 h of reflow, NC/Sn-3.5Ag might not form Cu₃Sn or the formation of Cu₃Sn is too little to be detected by XRD.

Figure 3.18 EDS compositional results of Cu₆Sn₅ in Figure 3.16 001 region

Figure 3.19 XRD pattern of NC/Sn-3.5Ag after reflow for 5 h at constant 230 °C.

After long time reflow, porous Cu_6Sn_5 will gradually be densified. Figure 3.20 shows densified Cu_6Sn_5 with porous Cu_6Sn_5 inside. Figure 3.16 (a) is the SEM Secondary Electron Image (SEI) of this structure. Figure 3.16 (b) shows the region (red square) analyzed by EDS, which revealed that the Cu at% in red square region is 42.01 while Sn at% is 57.99. By combination with the former XRD result in Figure 3.19, the IMC is Cu_6Sn_5 .

Figure 3.20 (a) SEM SEI of NC/Sn-3.5Ag interface after 2.5 hours of reflow, (b) EDS analyzed region

Figure 3.21 EDS compositional results of porous Cu_6Sn_5 in Figure 3.16 (b) red square region

In summary, SEM, EDS and XRD results are used to demonstrate the location, composition and phase of porous NC, Cu, Cu_6Sn_5 and porous Cu_6Sn_5 layers.

3.3.2 NC Spreading in Liquid Sn-3.5Ag Solder

One noticeable character of NC is its unique spreading behavior during the interfacial reaction with liquid-state Sn-3.5Ag. Besides the conventional understanding of diffusion between the solid Cu and liquid Sn-3.5Ag interface[67], NC will also spread into liquid solder in the form of particles or clusters, due to its porous structure and weak mechanical strength. This character affects the interfacial reaction of NC and Sn-3.5Ag.

In dense Cu and Sn-3.5Ag reaction, the diffusion coefficient of Cu into liquid-state Sn-3.5Ag (D_{Cu}) has already been obtained [58, 60, 68]. Ho's result stated that from 235 °C to 280 °C, the D_{Cu} is at the same order of magnitude ($10^{-9} \text{m}^2/\text{s}$) with a slight increase along with temperature rise.

Figure 3.22 (a) shows the spread NC particles in the molten solder. These particles moved into the liquid-state Sn-3.5Ag solder at 230 °C. After the solder solidified, they remained in the Sn-3.5Ag. The red ring area in Figure 3.22 (b) has been analyzed by EDS. The result is shown in Figure 3.23. These embedded NC particles has also been discovered in other reflow durations by other researchers [69, 70]. Considering the result in Figure 3.18 and other results [71], these are copper particles that have been detached from the sintered copper layer and dispersed into the molten solder during reflow.

Figure 3.22 (a) SEM BSI of NC/Sn-3.5Ag interface after 30s of reflow. (b) Higher magnification of embedded NC particles.

Figure 3.23 EDS compositional results of Red ring area in Figure 3.18 (b)

The weak consolidation in the sintered nano-copper layer may also result in a layer of NC to be detached, as shown in Figure 3.24. These detached particles or layers of particles will eventually react with Sn under extended reflow time.

Figure 3.24 SEM BSI of NC/Sn-3.5Ag interface after 30s of reflow.

As has been studied by Schnabl, the sintered NC has porous structure and nano-size grains [46]. This porous structure is not very dense and some of them have cracks on the surface. During the interfacial reaction, some part of the NC will be delaminated from the NC layer. Based on the experimental observation, it is reasonable to expect that these spread copper particles react faster with Sn-3.5Ag during reflow. This will be further investigated later.

In summary, the porous structure and nano-size grains of NC were observed, which leads to the distinct IMC morphology and distribution [72].

3.3.3 NC Surface Cracks

Another interesting character of this porous NC is its surface cracks. As mentioned before, the formed NC layer is porous after sintering. Cracks can be observed on its surface. The presence of cracks affects the interfacial reaction with Sn-3.5Ag.

Figure 3.21(a) illustrates the surface cracks on the NC layer. Figure 3.21 (b) shows the top view of the cracks on NC layer. Cu_6Sn_5 layer follows surface cracks, which means molten Sn has penetrated through the cracks to form Cu_6Sn_5 inside.

Figure 3.25 (a) SEM BSI of NC/ Sn-3.5Ag interface after 30s of reflow. (b) SEM image of surface cracks on NC layer.

In fact, it is common to find surface cracks on the NC surface. The cracks formation is influenced by the following factors: sintering condition, organic capping layer and solvents. It is not easy to form a NC layer without the formation of any cracks. The existence of some cracks accelerates the reaction between the NC metallization with solder.

3.3.4 IMC Morphology Difference between NC/Sn-3.5Ag and Cu/Sn-3.5Ag

According to experiment results, three IMC morphology differences between NC/Sn-3.5Ag and Cu/Sn-3.5Ag have been discovered. They are porous Cu_6Sn_5 , elongated Cu_6Sn_5 and Cu_3Sn .

First of all, porous Cu_6Sn_5 was found in NC/Sn-3.5Ag reaction while it was not found in Cu/Sn-3.5Ag reaction. Figure 3.11 and Figure 3.13 shows the cross-section morphology of Cu/Sn-3.5Ag reaction. Through SEM and XRD, Cu_6Sn_5 phase has been identified, but it does not have a porous structure. On the contrary, porous Cu_6Sn_5 can be found in Figure 3.14, Figure 3.15 and Figure 3.16. Porous Cu_6Sn_5 is a major morphology difference between NC/Sn-3.5Ag and Cu/Sn-3.5Ag.

It is known that porous Cu_6Sn_5 will be formed on the porous Cu and Sn interface after heat treatment and the formation of porous Cu_6Sn_5 is very quickly (around 10s on the certain condition) [73]. From the current experimental results, a quick formation of porous Cu_6Sn_5 is also found in Figure 3.16. Besides, through 5 h reflow, the porous Cu_6Sn_5 still remains in the NC/Sn-3.5Ag joint. A comparison between Cu_6Sn_5 and porous Cu_6Sn_5 is shown in Figure 3.26. It is obvious that porous Cu_6Sn_5 is present in NC/Sn-3.5Ag sample after 5 h of reflow at 230 °C, which dense Cu_6Sn_5 is present in the plated dense Cu/Sn-3.5Ag reaction.

Figure 3.26 SEM SEI of Cu_6Sn_5 formed after 5 h of reflow at 230 °C (a) Cu/Sn-3.5Ag (b) NC/Sn-3.5Ag.

After 5 min of interfacial reaction, elongated Cu_6Sn_5 appears in NC/Sn-3.5Ag samples. The IMCs in Cu/Sn-3.5Ag samples, however, still remain scallop-type without large elongation. For example, from Figure 3.13 (a) to Figure 3.13 (j), IMCs in Cu/Sn-3.5Ag starts from small scallop-type grain to big scallop-type grain without obvious elongation. However, in Figure 3.14 (d) to Figure 3.14 (j), elongated Cu_6Sn_5 are found. The corresponding SEM images of top-view morphology also demonstrate the existence of the elongated Cu_6Sn_5 (shown in Figure 3.15 (d) to (h)). Besides, this elongated Cu_6Sn_5 shows a hexagonal shape (Figure 3.27 (a), (b)).

Figure 3.27 SEM image of hexagonal Cu_6Sn_5 in NC/Sn-3.5Ag after 40 min of reflow (a) top-view, (b) cross-section

The explanation of this elongated Cu_6Sn_5 is as follows. The Cu_6Sn_5 phase has a hexagonal structure B8_1 NiAs type structure[74]. The growth of hexagonal Cu_6Sn_5 is followed by screw dislocation along the long axis of the elongated structure[75]. On the NC/Sn-3.5Ag interface, the spreading of NC in liquid Sn-3.5Ag solder may have caused detachment of the IMC to grow in a surrounded molten Sn environment, which is different from the attached IMC in the case of dense Cu metallization. Nevertheless, the IMCs closely attached to the NC metallization layer still remains scallop-type Cu_6Sn_5 . The anisotropic growth of Cu_6Sn_5 leads to the elongated Cu_6Sn_5 due to different Cu_6Sn_5 growth rates along different crystalline directions [76]. Therefore, grains oriented along the fast growing direction grow up to larger thickness than grains to other directions [72]. However, when the IMC grows at the IMC/Cu substrate, the limiting factor for the growth is the supplier of Cu through the IMC, therefore the surface morphology is governed by the minimization of the surface energy and interface energy.

Figure 3.28 Schematic diagram illustrating the growth of the hexagonal Cu_6Sn_5 using the proposed screw dislocation ledge mechanism model [75].

Third, Cu_3Sn was not found in NC/Sn-3.5Ag. According to the cross-section image in Figure 3.14(j), top view image in Figure 3.15(h) and XRD pattern in Figure 3.19, after 5 h of reflow, Cu_3Sn was not formed in the NC/Sn-3.5Ag reaction couple. However, a clear layer of Cu_3Sn is found in Figure 3.11 for the plated Cu/Sn-3.5Ag reaction couple. It was reported that Cu_6Sn_5 and Cu_3Sn are able to transform into each other [77]. The transformation between these two phases depends on the concentration and diffusion of Cu and Sn. In Cu/Sn-3.5Ag, the formation of dense scallop-type Cu_6Sn_5 layer obstruct the supply of Sn, as a result, the Cu_6Sn_5 layer will transform in Cu_3Sn on the Cu side [10]. In NC/Sn-3.5Ag, porous NC and porous Cu_6Sn_5 provide channels for liquid Sn. And NC will also spread very fast in liquid Sn. As a result, the Cu_6Sn_5 to Cu_3Sn transformation did not occur. Besides, even if some Cu_3Sn formed during the NC/Sn-3.5Ag reaction, a reverse transformation from Cu_3Sn to Cu_6Sn_5 [78] will also consume this newly formed Cu_3Sn . Therefore, no Cu_3Sn has been observed in NC/Sn-3.5Ag.

3.3.5 IMC Growth Mechanism in NC/Sn-3.5Ag

Since the IMC morphology of NC/Sn-3.5Ag is quite different from Cu/Sn-3.5Ag, it is necessary to understand the IMC growth mechanism in NC/Sn-3.5Ag. A schematic explanation of NC and Sn-3.5Ag interfacial reaction is illustrated in Figure 3.29.

The reaction process is as follows. At the beginning of the interfacial reaction (Figure 3.29 (a)), numerous small scallop-type Cu_6Sn_5 is formed on the porous NC and Sn-3.5Ag interface. Since the formation of these Cu_6Sn_5 is a result of reaction with porous NC, some of them retain the porous structure. In Figure 3.29 (b), the scallop-type Cu_6Sn_5 layer becomes much thicker and denser with the reaction time. Beneath the scallop-type Cu_6Sn_5 , the initial porous Cu_6Sn_5 still remains. As the reflow continues, shown in Figure 3.29 (c), small scallop-type grains start to ripen. In other words, scallop-type Cu_6Sn_5 starts to grow bigger at the expense of its smaller neighbors. Besides, more and more NC has been consumed. Once the porous NC layer has been consumed, the bottom sputtered Cu start to join the interfacial reaction (As it is shown in Figure 3.14 from (a) to (e), the bottom sputtered Cu still remained the same thickness, but from Figure (f) to (j), the bottom sputtered Cu gradually became thinner and thinner). At around the stage shown in Figure 3.29 (d), the interfacial reaction between NC and Sn-3.5Ag slows down due to the consumption of NC. Some ripened Cu_6Sn_5 on Sn side of the interface starts to spall off. As it is illustrated in Figure 3.29 (e), the ripening and elongation of Cu_6Sn_5 continues. In the end, after 5 hours of reflow, the NC/Sn-3.5Ag interfacial reaction forms a thick IMC layer, which contains initial porous Cu_6Sn_5 and dense Cu_6Sn_5 (Figure 3.29 (f)).

Figure 3.29 Schematic of NC and Sn-3.5Ag interfacial reaction.

The whole process could be classified into two main stages. The first stage is fast consuming NC (from (a) to (c)). The second stage is IMC ripening and elongation (from (d) to (f)).

At the first stage, the fast consumption of NC is because of the large Cu surface area derived from its porous structure and surface cracks. As a result, from Figure 3.14, we can barely find NC after around 1 hour interfacial reaction.

At the second stage, the elongation and ripening of IMCs in NC/Sn-3.5Ag is different from the IMCs in Cu/Sn-3.5Ag. First of all, the elongation of IMCs in NC starts earlier and their elongation is more obvious (Figure 3.14) than IMCs in dense Cu (Figure 3.13). As it was studied before, for the purpose of compensating the reduction of Cu channels caused by IMC growth, the Cu_6Sn_5 elongated their grains[10]. Since NC has a porous structure, the reduction of Cu channels could be more serious than dense Cu. Therefore, IMCs in NC shows more aggressive elongation behavior. Second, spalling happens in the NC/Sn-3.5Ag interface. In dense Cu, according to K.N. Tu et al., as long as free Cu exists in the UBM, Cu_6Sn_5 compound will stick to the free Cu and will not spall[56]. However,

in NC, interface IMCs will spall off even though free NC still exists. This unique spalling behavior is caused by the porous structure of NC. Since the formation of IMCs in NC/Sn-3.5Ag is on the foundation of porous NC, the IMCs are not dense either. They may easily detach from the interface. Third, the growth of IMCs in NC/Sn-3.5Ag reaction is provided by both the interfacial NC and detached NC. According to Ostwald ripening theory, which is described by Wilhelm Ostwald in 1896[79], in solid solutions, small crystals will redeposit onto larger crystals over time. During the reflow experiment, instead of forming the IMCs at the interface, several spread NC forms small IMCs in liquid state reaction with Sn-3.5Ag. However, compared to the interface IMCs, these small IMCs are not very stable. Once the interface IMCs contact with these small IMCs, they tend to join together to decrease the surface energy (ripening). As a result, instead of interface NC, the spread NC also contribute to the IMCs growth.

3.3.6 IMC Growth Kinetic Analysis

According to previous kinetic analysis of Cu/Sn, the thickness of IMCs has an empirical power law with the reflow time [10, 57, 61]. The equation (1) explains this relationship.

$$\delta = k_1 t^{1/n} \quad (1)$$

where δ is the thickness of IMCs, t is the reflow time, n is the time exponent and k_1 is the grow rate constant.

To quantify the growth thickness of Cu_6Sn_5 , the experimental data of NC/Sn-3.5Ag and Cu/Sn-3.5Ag interfacial reactions are curve-fitted into the equation (1). The result is shown in Figure 3.30. The best fit of all experimental data describing the thickening kinetics is listed in Table 3.1.

The equation (1) can be Logarithm transformed to Equation (2).

$$\text{Log } \delta = \text{log } k_1 + (1/n) \text{ log } t \quad (2)$$

In the Equation (2), $1/n$ is obtained by the slope in Figure 3.30 and $\text{log } k_1$ equals to the intercept. The results in Table 3.1 show that $n_{(\text{Cu})} = 3.166$ is greater than $n_{(\text{NC})} = 2.159$. Besides, as we mentioned before (3.2 Experimental Procedure) that both NC/Sn-3.5Ag and Cu/Sn-3.5Ag samples went through the same reflow condition and the only difference is whether the under bump metallization is NC or Cu, therefore, according to

results in Figure 3.30 and Table 3.1, we conclude that the interfacial reaction of NC/Sn-3.5Ag is faster than Cu/Sn-3.5Ag.

Figure 3.30 Log-log plot of Cu_6Sn_5 thickening kinetics during liquid-state reaction

Table 3.1 Kinetics Parameters for the Growth of Cu_6Sn_5 IMC in Sn-3.5Ag with NC and Cu during Liquid-State Reaction

UBM	k_1	n	$1/n$
NC	0.391	2.159	0.463
Cu	0.589	3.166	0.315

Cu/Sn-3.5Ag liquid-state reaction has already been studied before[10, 52, 53, 55, 57, 58, 61]. From previous results, we found that n ranges from 2.5 to 4 for the similar solid-liquid state interfacial reaction. K. N. Tu et al. found that the IMC mean grain radius follows the $t^{1/3}$ growth law[10]. Matt Schaefer mentioned that IMC growth between Cu and 62Sn36Pb2Ag solder exhibits $t^{1/4}$ dependence on time t . Won Kyoung Choi's results implied that IMC growth in Cu/Sn-3.5Ag liquid-state interfacial reaction follows the $t^{0.4}$

growth law. All in all, the reported n of the Cu/Sn-3.5Ag liquid-state interfacial reaction is around 2.5 to 4.

For the purpose of explaining the empirical power law of IMC growth, some kinetics models based on Fick's Law have been introduced [55, 59]. As for Cu/Sn-3.5Ag liquid-state interfacial reaction, it was explained that the reaction is controlled by volume diffusion and interfacial reaction[55]. Both two factors lead to the related $t^{1/3}$ law. In the current work, the observed scallop morphology suggests that the IMC growth in the case of Cu/Sn-3.5Ag is likely to be controlled by diffusion through the IMC grooves as described by K.N. Tu et al. [10].

However, Schaefer and K. L. Erickson proposed that if the IMC growth is diffusion-limited condition, the n should be around 2 [57, 59]. The diffusion-limited condition means that the diffusion is the slowest step and thus limits the whole reaction. According to Erickson's model, which is based on a one-dimensional, multilayer system involving a binary set of interacting constituent model and deduced from material balance equation and interfacial displacement equation of different layer, the displacement of each interface or the IMCs growth thickness can be given by

$$\delta(t)=2\gamma \sqrt{D t} \quad (3)$$

where $\delta(t)$ is the IMC thickness, γ is variable related to w (mass fraction of different layers) and D (a variable diffusion coefficient)[59]. Because the n value of NC/Sn-3.5Ag is 2.159, which is close to 2, it is reasonable to deduce that the NC/Sn-3.5Ag interfacial reaction is a diffusion-limited reaction. The limiting factor of the reaction speed is the initially formed Cu_6Sn_5 IMC layer. This implies that the chemical reaction between NC and Sn-3.5Ag is so fast that the final IMC formation speed is not limited by this reaction.

3.4 Conclusion

The sintered NC has a porous nanocrystal structure with some cracks on its surface. The morphology of NC influences its interfacial reaction with Sn-3.5Ag. The cross-sectional morphology between Cu-3.5Ag and NC/Sn-3.5Ag is compared. Porous Cu_6Sn_5 is found in NC/Sn-3.5Ag interfacial reaction. Besides, different from dense plated Cu, NC has a distinguishing spreading behavior in liquid state Sn-3.5Ag solder, which leads to formation of elongated Cu_6Sn_5 . Based on the SEM and EDS data, NC and Sn-3.5Ag

interfacial reaction mechanism has been explained. Kinetic analysis of NC/Sn-3.5Ag and Cu/Sn-3.5Ag reveals that NC/Sn-3.5Ag reaction is faster than Cu/Sn-3.5Ag. Furthermore, NC/Sn-3.5Ag reaction is limited by diffusion through a continuous IMC layer, while Cu/Sn-3.5Ag is a reaction controlled by both diffusion fast diffusion grooves between IMC grains.

Chapter 4 Adhesion study between NC and different metallizations

Introduction

NC as a soldering metallization has been studied in Chapter 3. Besides being a special metallization, NC paste is also a potential candidate for joining different electronic components. As it is mentioned earlier that NC has many advantages, like low melting point and good thermal and electrical conductivity while having relatively cheap price. For the purpose of its potential as a joining material used in the future, it is essential to understand its adhesion conditions with other metallization surfaces. Different metallizations, which are either commercialized or the ones have very good performance for lead-free soldering, were prepared. Adhesion between NC and different metallizations is studied in this chapter.

ASTM Cross-cut Tape Adhesion Test D3359 and die shear test were carried out to exam the adhesion between NC and different metallizations. The metallizations includes Cu, Cr/Ni/Au, Electroless Nickel Immersion Gold (ENIG), Electroless Nickel (EN), Ni-Sn-P, Ni-W-P and Ni-Co-P. Scanning Electron Microscope (SEM) was utilized to analyze the sheared substrate, and the failure mechanism was investigated.

4.1 Experimental Procedure

The experimental procedure consists of four parts. The first part is to make different metallizations. They are Cu, Cr/Ni/Au, ENIG, EN, Ni-Sn-P, Ni-W-P and Ni-Co-P metallization. Then the analysis of prepared metallizations was conducted with SEM, EDS and AFM. After analyzing these metallizations, cross-cut adhesion test and die shear

test were prepared and carried out. The final step is the fractographic analysis of the sheared substrate.

4.1.1 Sample Preparation

As it was mentioned in 2.1.2 Packaging Metallization, metallization is a critical part in packaging especially for its reliability. Cu, Cr/Ni/Au, ENIG, EN, Ni-Sn-P, Ni-W-P and Ni-Co-P metallizations are chosen for the following reasons.

To start with, as NC is utilized as a solder material, there is no reliability problem of IMC growth since Cu solder and Cu substrate will not form any IMC. However, the joint strength may be a concern and thus should be studied. As for Cr/Ni/Au, it is a traditional tri-layer metallization. The function of these different layers is explained in 2.1.2 Packaging Metallization. They are compared with ENIG, one of the most predominated metallization used for printed circuit boards. Whether NC has good adhesion with this metallization affects NC's potential as a soldering (or joining) material. EN (Electroless Nickel) is an intermediate product of ENIG during the surface finish process. Comparing EN and ENIG, the function of immersion gold layer could be revealed. Ni-Sn-P, Ni-W-P and Ni-Co-P were researched recently as new metallization materials [80-82] for lead-free solder application. They are studied in comparison with binary Ni-P alloy.

To prepare these metallizations, different processes were used. Cu metallization formed by sputtering. The silicon wafers surface were cleaned by the AMI procedure[63] first before putting them into Kurt J Lesker PVD 75 chamber to sputter a layer of 2 μ m Cu. These Cu wafers were also used as a substrate for ENIG and EN samples. Cr/Ni/Au also formed by sputtering. The layer of Cr is around 0.1 μ m followed by 1 μ m Ni and 0.3 μ m Au.

Sputtered Cu wafers were cleaned by acetic acid (99.7%) to remove the oxidation layer [83]. Then the surface was activated using a commercial ruthenium-based Pre-initiator at 43 °C for 4 min. Electroless Nickel Plating was conducted in a commercial acidic sodium bath (from MacDermid) with a pH level of 5.1 at 88 $\pm$ 2 °C for 1 hour. As for ENIG, an extra step, Immersion Gold, was added after the electroless Ni plating. A non-cyanide immersion gold solution named Supermex #250 was used to immerse a thin layer of gold on the EN with a pH level of 7 $\pm$ 0.5 at 70 °C for 10 min.

The procedure for making Ni-Sn-P, Ni-W-P and Ni-Co-P is slightly different. Cu plates (99.98 wt%) with a thickness of 6 mm were used as a substrate for Ni-Sn-P, Ni-W-P and Ni-Co-P electroless plating. The plating baths are shown in Table 4.1. Electroless Ni-Sn-P plating was performed in alkaline bath at pH 9.0 and 88 ± 2 °C for 30 min [84]. Electroless Ni-W-P plating was conducted in alkaline bath with a pH level of 9.0 (adjusted by 25% sulphuric acid) at 85 ± 2 °C for 2 h. The electroless Ni-Co-P plating was carried out in alkaline bath with a pH level of 10.0 at 88 ± 2 °C for 1 h [80-82]. The formation processes of these different metallizations are illustrated in Table 4.2.

Table 4.1 Composition of the plating bath for Ni-Sn-P, Ni-W-P and Ni-Co-P [80-82]

Ni-Sn-P	
Constituents of plating bath	Concentration
NiSO ₄ ·6H ₂ O	20 g/L
SnCl ₂ ·2H ₂ O	1 g/L
NaH ₂ PO ₂ ·H ₂ O	20 g/L
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	35 g/L
(NH ₄) ₂ SO ₄	30 g/L
Lactic acid	4 mL/L
Ni-W-P	
Constituents of plating bath	Concentration
NiSO ₄ ·6H ₂ O	26 g/L
Na ₂ WO ₄ ·2H ₂ O	33 g/L
NaH ₂ PO ₂ ·H ₂ O	12 g/L
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	75 g/L
Ni-Co-P	
Constituents of plating bath	Concentration
NiCl ₂	10 g/L
CoCl ₂	4 g/L
NaH ₂ PO ₂ ·H ₂ O	16 g/L
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	40 g/L
NH ₄ Cl	30 g/L
Lactic acid	4.5 mL/L

Table 4.2 Summary of different metallization formation methods

Metallization	Formation Methods
Cu	Sputtering
Cr/Ni/Au	Sputtering
ENIG	Electrochemical
EN	Electrochemical
Ni-Sn-P	Electrochemical
Ni-W-P	Electrochemical
Ni-Co-P	Electrochemical

4.1.2 Metallization Analysis

Once the different metallizations were prepared, they went through scan using Atomic Force Microscope (AFM) to evaluate the surface morphology, SEM and EDS to test the element concentration of the metallization cross-section and XRD to verify the phases.

To prepare for the AFM test, different metallizations samples were cut into small pieces. Then they were put into Asylum Research MFP-3D to obtain detailed morphological information. The Asylum Research MFP-3D is in tapping/non-contact mode at room temperature and in air. The scan area is $10 \times 10 \mu\text{m}^2$. Surface roughness R_q of different metallizations surface was also recorded.

As for SEM test, different metallizations samples were cold mounted in epoxy and then grinded and polished to reveal the cross-sectional layer of the metallization. After that, these polished samples were coated with a 20 nm layer of Au to prevent charging in SEM. The SEM equipment used in this experiment is JEOL 6360.

Bruker D8 Advance was utilized to obtain XRD patterns. The voltage used is 40 kV and current is 40 mA. The scan speed is 0.5s/step with 2 degree insert angle.

4.1.3 Preparation of Adhesion Test Sample

The prepared metallization substrates were cut into small pieces, and then followed with regular cleaning procedure. The schematic structure of the cross-cut adhesion test sample is shown in Figure 4.1.

Figure 4.1 Schematic structure of the cross-cut adhesion test sample

For the cross-cut adhesion test, the metallization is Meyer bar coated with a layer of NC paste and then sintered at reflow furnace following the same reflow curve shown in Figure 3.10. This sintering process is in the N_2 atmosphere. The ramping up speed is around $11.5\text{ }^{\circ}\text{C}/\text{min}$. The duration time is 10 min at $230\text{ }^{\circ}\text{C}$. After reflow, the samples were gradually cooled in the oven at $2.67\text{ }^{\circ}\text{C}/\text{min}$. At around $150\text{ }^{\circ}\text{C}$, the oven is cooled with flowing water and the samples are taken out at room temperature.

For the shear test sample, a sandwich structure is formed. The Cu coated Si die on the top is $1*1\text{ mm}^2$. Different metallizations are on the bottom. The schematic structure is shown in Figure 4.2. Following the same procedure as for the cross-cut adhesion test, shear test sample also uses Meyer bar to coat a layer of NC paste and the joining was carried out in N_2 atmosphere. The joining process basically follows the same as NC sintering procedure as described in section 3.2.1. Three different peak holding temperatures were used at 230, 260 and $290\text{ }^{\circ}\text{C}$.

Figure 4.2 Schematic structure of the shear test sample

4.1.4 Cross-cut Adhesion Test and Shear Test

Cross-cut adhesion test and shear test were carried out once the samples were prepared. According to ASTM Tape Test Standard D3359-09, the cross-cut adhesion test was used to measure the extent of adhesion of the coatings to the substrate [85-87]. The adhesion test samples went through cross-cut adhesion test first to roughly evaluate their adhesion with NC. Metallizations having comparable adhesion with NC went through shear test to obtain quantified adhesion strength information.

In the industry, the adhesion of the coating is evaluated by paint adhesion testing, which involves three different tests: cross-cut, scrape and pull-off tests. In this experiment, cross-cut test was used. Generally, the procedure of the cross-cut adhesion test includes three parts: cut and cross-cut, tape stick and remove, and finally evaluation. Cut and cross-cut is to make crossed grids on the metallization surface. Tape stick and remove is to use a special tape to stick on the cut surface and remove the tape. The evaluation is to compare the tested samples with the standard. The classification of tape adhesion test results is shown in Figure 4.3, which explains a standard method used to quantify the extent of adhesion between coating and substrate. Grades of adhesion are classified into 5 levels: 5B, 4B, 3B, 2B, 1B and 0B, where coating rated 5B exhibit the highest adhesion and 0B the poorest adhesion.

CLASSIFICATION OF ADHESION TEST RESULTS		
CLASSIFICATION	PERCENT AREA REMOVED	SURFACE OF CROSS-CUT AREA FROM WHICH FLAKING HAS OCCURRED FOR SIX PARALLEL CUTS AND ADHESION RANGE BY PERCENT
5B	0% None
4B	Less than 5%
3B	5 - 15%
2B	15 - 35%
1B	35 - 65%
0B	Greater than 65%

Figure 4.3 Classification of adhesion test results[85]

Shear test is widely used in measuring the shear strength of die-attach joint. In this experiment, the shear test was performed in DAGE 4000 with shear speed of 10 $\mu\text{m/s}$, shear load of 5 kg and shear height of 15 μm . The schematic illustration of the die shear testing setup is shown in Figure 4.4. According to the Mil-Std-883 standard, the stress direction of applied force, $\vec{F}$ (Figure 4.4), should be parallel to the die attach substrate [88, 89].

During the shear test, the top die will detach from the bottom part once the maximum force is reached. In order to acquire relatively precise shear strength, flexible clamps were used to hold the specimen to avoid twisting the joint. To avoid experimental error, 10 shear test samples were made for each type of metallization sample.

Figure 4.4 The schematic illustration of the die shear testing setup[90]

After the shear test, the shear force $\vec{F}$ results in the form of weight (g) for different shear test samples were obtained. The shear strength τ is calculated by Equation (4), where F is the maximum shear force and A is the contact area between the top die and the substrate [91].

$$\tau = F/A \quad (4)$$

The shear strength values of $1 \times 1 \text{ mm}^2$ dies were calculated with equation (4).

4.1.5 Microstructure Observation

After cross-cut adhesion test, samples were observed by optical microscope. Grade of adhesion was given according to D3359-09 specifications.

Before the shear test, some shear test samples were cold mounted in epoxy and polished to reveal the cross-section. SEM6360 was used to analyze the cross-section of prepared shear test samples. After shear test, the sheared substrate was analyzed by SEM6360. The failure mode of the sheared samples was classified by referring to failure mode classification carried out by Chai TC group [92]. The category of failure mode is shown in Figure 4.5. The bulk failure resulted in higher failure strength. IMC failure and pad peeling (delamination) reveal lower failure strength. Due to the complexity of different cases, some failure may be the combination of these three types.

Figure 4.5 Failure mode observed from shear test [92]

4.2 Results and Discussion

4.2.1 Different Metallizations

SEM, EDS and AFM results of different metallizations are shown separately. Their surface roughness based on AFM is compared.

Figure 4.6 shows Ni-P metallization and its AFM image. The surface roughness R_q of the Ni-P metallization is 63.9 nm. Figure 4.7 shows Ni-P cross-sectional BSI and EDS results, which reveals that Ni-P layer is around 8 μm thick and contains 4.26 at% phosphorus.

Figure 4.6 Ni-P metallization and its AFM image

Figure 4.7 BSI and EDS result of Ni-P cross-section

Figure 4.8 shows Ni-Co-P metallization and its AFM image. The surface roughness R_q of the Ni-Co-P metallization is 64.5 nm. Figure 4.9 shows Ni-Co-P cross-sectional BSI and EDS result, which reveals that Ni-Co-P layer is around 7 μm thick and contains 18.40 at% phosphorus and 18.27 at% cobalt.

Figure 4.8 Ni-Co-P metallization and its AFM image

Figure 4.9 BSI and EDS result of Ni-Co-P cross-section

Figure 4.10 shows Ni-W-P metallization and its AFM image. The surface roughness R_q of the Ni-W-P metallization is 53.2 nm. Figure 4.11 shows Ni-W-P cross-sectional BSI and EDS result, which reveals that Ni-W-P layer is around 12 μm in thickness and contains 16.36 at% phosphorus and 4.66 at% tungsten.

Figure 4.10 Ni-W-P metallization and its AFM image

Figure 4.11 BSI and EDS result of Ni-W-P cross-section

Figure 4.12 shows Ni-Sn-P metallization and its AFM image. The surface roughness R_q of the Ni-Sn-P metallization is 115.9 nm. Figure 4.13 shows Ni-Sn-P cross-sectional BSI and EDS result, which reveals that Ni-Sn-P layer is around 11 μm in thickness and contains 12.86 at% phosphorus and 12.31 at% tin.

Figure 4.12 Ni-Sn-P metallization and its AFM image

Figure 4.13 BSI and EDS result of Ni-Sn-P cross-section

Figure 4.14 shows Cr/Ni/Au metallization and its AFM image. The surface roughness R_q of the Cr/Ni/Au metallization is 10.7 nm. Figure 4.15 shows Cr/Ni/Au cross-sectional BSI and Figure 4.16 shows Cr/Ni/Au EDS element mapping result, which reveals that the thickness of Cr layer is around 1 μm , Ni layer is around 1 μm and Au layer is around 0.3 μm .

Figure 4.14 Cr/Ni/Au metallization and its AFM image

Figure 4.15 BSI result of Ni-Sn-P cross-section

Figure 4.16 EDS element mapping analysis of Cr/Ni/Au & NC interface

Figure 4.17 shows ENIG metallization and its AFM image. The surface roughness R_q of the Cr/Ni/Au metallization is 7.3 nm. Figure 4.19 shows ENIG cross-sectional BSI and EDS result, which reveals that Ni-P layer is around 5 μm in thickness and contains 4.26 at% phosphorus and Au layer is around 250 nm.

Figure 4.17 ENIG metallization and its AFM image

Figure 4.18 BSI and EDS result of ENIG cross-section

The surface roughness of different metallizations was compared in Figure 4.19. In this experiment, the root mean squared surface roughness (R_q) is chosen as the parameter to reflect surface roughness of different metallizations. Cu, ENIG, Cr/Ni/Au are relatively smoother than other metallizations. Ni-Sn-P is the roughest metallization.

Figure 4.19 Surface roughness of different metallizations

4.2.2 Cross-cut Adhesion Test

The cross-cut adhesion test results of NC and different metallizations are shown in Figure 4.20. The experiment results were compared with the classification based on ASTM Tape Test Standard D3359-09, which is shown in Figure 4.3. From the result, Cu/NC and ENIG/NC have the best adhesion, which is classified as 3B. The Ni-P, Ni-Co-P, Ni-W-P do not have good adhesion with NC. Their adhesion results are 1B or 0B.

Experiment Result	Classification	Percent Area Removed	Surface of cross-cut area from which flaking has occurred for six parallel cuts and adhesion range by percent
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3B	5 - 15%		
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2B	15 - 35%		
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2B	15 - 35%		
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3B	5 - 15%		
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Figure 4.20 Cross-cut adhesion test of NC and different metallizations, (a) Cu (b) Cr/Ni/Au/NC (c) Ni-Sn-P (d) ENIG (e) Ni-P (f) Ni-Co-P (g) Ni-W-P (h) Cu with CuO

Presence of CuO will largely affect the adhesion between NC/Cu. Figure 4.20 (h) shows the cross-cut adhesion result between Cu and NC. The Cu with CuO condition was prepared without cleaning the Cu surface with acetic acid, so that a layer of CuO will remain on the Cu substrate. The adhesion between NC and Cu with CuO is classified into 1B. This oxidation layer has largely decreased the adhesion between NC and Cu.

The cross-section SEM images of Ni-Co-P, Ni-P and Ni-W-P die-attach joint are shown in Figure 4.21, Figure 4.22 and Figure 4.23. The cross-section image reveals that the sintered NC in the die-attach sample is very porous and even have some cracks. Some delamination between metallization and NC is detected. It is these cracks and

delamination that causes the bad adhesion performance of Ni-P, Ni-Co-P and Ni-W-P. Figure 4.24 shows the cross-section SEM images of ENIG/NC die-attach joint, which shows that NC layer is more compact than other Ni-P, Ni-Co-P and Ni-W-P. Besides, no obvious cracks are detected in NC/ENIG.

Therefore, better densification of NC and good Au/NC adhesion are the causes of good cross-cut adhesion test result of NC/ENIG. The poor cross-cut adhesion test result is due to more porous NC layer, and presence of cracks and delamination.

Figure 4.21 SEM BSI of NC/Ni-Co-P joint

Figure 4.22 SEM BSI of NC/Ni-P joint

Figure 4.23 SEM BSI of NC/Ni-W-P joint

Figure 4.24 SEM BSI of NC/ENIG joint

4.2.3 Shear Test

Based on the results of cross-cut adhesion test in 4.2.2, Cu, ENIG, Cr/Ni/Au, Ni-Sn-P are chosen for shear test. The shear test results of these four metallizations die-attach joints at 230 °C, 260 °C and 290 °C are shown in Figure 4.25.

The results in Figure 4.25 reveal that the shear strength becomes stronger with the increase of sintering temperature. Besides, Cu/NC has the strongest shear strength among these four kinds of die shear joints. The big variation of the error bars in Figure 4.25 is due to sample disturbance and shear test itself. In this experiment, the shear test samples were prepared by sintering without uniform pressure, which contributes to the non-uniform fusing of the NC. Failure planes will propagate through the weakest part in this non-uniform fused NC interface in the shear test. Therefore the shear strength variation could be very high from sample to sample.

However, the shear strength of Cu/NC and ENIG/NC at 290 °C is lower than its at 260 °C. This could be due to partial oxidation of the NC. Even though the experiment is conducted in N₂ atmosphere, some O₂ still remains in the furnace chamber. These residual O₂ reacted with NC to form red color Cu₂O, which reduced the shear strength of the die shear joints.

For the overall strength for the Ni-Sn-P/NC joint is low at all joining temperatures. Whether Ni-Sn-P and NC formed any kind of metallization reaction remains to be studied. Based on the current work, it is found that it does not adhere with NC well.

Figure 4.25 Shear test results of NC/Cu, NC/Cr/Ni/Au, NC/ENIG, and NC/Ni-Sn-P (230 °C, 260 °C and 290 °C). Error bars indicate standard deviation on 10 samples of each type of metallization.

In order to further understand failure modes of the shear test results, SEM was utilized to analyze the sheared bottom substrate. Figure 4.26 shows SEM SEI of sheared substrates of NC/Cu, NC/Cr/Ni/Au, NC/ENIG and NC/Ni-Sn-P. Figure 4.26(a) shows that the Cu densification is better than another three metallizations and no delamination is found in NC/Cu joint. By referring to Figure 4.5 the failure mode reference, NC/Cu is classified into bulk failure.

Obvious delamination can be observed in Figure 4.26(b) NC/Cr/Ni/Au sheared substrate. It is the delamination between NC and Cr/Ni/Au causes the relatively low shear strength of NC/Cr/Ni/Au joint. By referring to Figure 4.5, NC/Cr/Ni/Au is classified into bulk-partial pad peeling failure. The pad peeling or delamination is an indication of weaker pad to core substrate interface integrity [92]. Since the shear speeds of these of metallizations are the same. The cause of this delamination lies with the different metallizations.

Figure 4.26 SEM SEI of sheared substrates (a) NC/Cu, (b) NC/Cr/Ni/Au, (c) NC/ENIG, (d) NC/Ni-Sn-P.

Figure 4.26(c) reveals that the adhesion between NC/ENIG is strong enough to avoid delamination. However, small part of delamination can also be detected from the SEM image. Therefore, the classification of NC/ENIG belongs to bulk-partial pad peeling failure.

From Figure 4.26(d) NC/Ni-Sn-P SEM secondary electron image (SEI), a serious delamination between NC and Ni-Sn-P is found. For the purpose of better understanding NC/Ni-Sn-P reaction, element mapping of this sheared substrate was carried out. Figure 4.27 shows the element mapping of NC/Ni-Sn-P sheared substrate, which implies that NC does not react with Ni-Sn-P. The further verification of assumption was done by XRD. Figure 4.28 shows the XRD pattern of NC/Ni-Sn-P sheared substrate. This result testified that no IMC has been generated between NC and Ni-Sn-P. By combination with the AFM surface roughness result (shown in Figure 4.19) the surface roughness of the

Ni-Sn-P should have positive affect on the relatively good adhesion of the NC/Ni-Sn-P. Therefore, the failure mode of NC/Ni-Sn-P is classified as bulk-partial pad peeling failure.

Figure 4.27 Element mapping of NC/Ni-Sn-P sheared substrate

Figure 4.28 XRD pattern of NC/Ni-Sn-P sheared substrate

In conclusion, according to shear test results, Cu has the strongest adhesion with NC. By fractographic analysis of the sheared substrate, Cu/NC failure mode is defined as bulk cohesive NC failure, which resulted in higher failure strength. While the failure modes of NC/Ni-Sn-P NC/Cr/Ni/Au, NC/ENIG are defined as bulk-partial pad peeling failure.

4.3 Conclusion

In conclusion, different metallizations, Cu, Cr/Ni/Au, ENIG, EN, Ni-Sn-P, Ni-W-P and Ni-Co-P are prepared. The cross-cut adhesion study between sintered NC and different metallizations reveals that NC, ENIG, Cr/Ni/Au and Ni-Sn-P has comparably good adhesion (2B-3B) while Ni-P, Ni-Co-P and Ni-W-P do not adhere to sintered NC very well (0B-1B). Besides, it was found that the copper oxidation would seriously affect Cu/NC adhesion. The result of the shear test results reveal that Cu/NC has better adhesion compared with another three metallizations. NC/Cu failure mode is bulk cohesive failure resulted in higher failure strength. The failure modes of Ni-Sn-P/NC, Cr/Ni/Au and ENIG are bulk-partial pad peeling.

Chapter 5 Conclusions and Future Work

5.1 Conclusions

The main objective of this work was to investigate the electronic packaging applications for Nano-Copper (NC). In this work, two kinds of applications were studied: NC as a solder metallization and NC as a die attach (joining) material. For a complete understanding, several process parameters and materials, such as NC sintering parameters, reflow time spans, different metallizations, were varied systematically and their relationship with the NC performance was studied. From this work, the following conclusions could be drawn:

The optimal sintering condition of the NC paste has been determined. After sintering, NC will form a porous nanocrystal structure. This structure inevitably contains some cracks. The properties of sintered NC as a solder metallization with Sn-3.5Ag solder have been studied. By comparing interfacial reaction between Cu/Sn-3.5Ag and NC/Sn-3.5Ag, morphology and kinetic differences are discovered. In the morphology study, NC/Sn-3.5Ag forms porous Cu_6Sn_5 and some Cu_6Sn_5 have elongated shape. The Cu/Sn-3.5Ag reaction reveals scallop-type Cu_6Sn_5 only, in good agreement with previous studies. Besides, NC's distinguishing spreading behavior in liquid Sn-3.5Ag solder affects the formation of Cu_3Sn in NC/Sn-3.5Ag. No obvious Cu_3Sn was found in NC/Sn-3.5Ag while an obvious layer of Cu_3Sn was found in Cu/Sn-3.5Ag. Through analyzing the morphology data, an Intermetallic compounds (IMC) growth mechanism in NC/Sn-3.5Ag was put forward, which explains the IMC growth process in detail. In kinetic study, $t^{1/3}$ growth kinetics was discovered in Cu/Sn-3.5Ag while $t^{1/2}$ growth kinetics was discovered in NC/Sn-3.5Ag. This result gives a quantitative conclusion that the reaction in NC/Sn-3.5Ag is faster than Cu/Sn-3.5Ag. Besides, based on other researchers' study, NC/Sn-3.5Ag interfacial reaction is deduced to be diffusion-limited by fast diffusion channels, while Cu/Sn-3.5Ag interfacial reaction is a reaction controlled by diffusion of a continuous IMC layer.

NC's die attach joining application was studied through adhesion study between NC and different metallizations. Metallizations were prepared by either sputtering or electrochemical method. The cross-cut adhesion study between sintered NC and different

metallizations reveals that NC, ENIG, Cr/Ni/Au and Ni-Sn-P has comparably good adhesion (2B-3B) while Ni-P, Ni-Co-P and Ni-W-P do not join sintered NC very well (0B-1B). Besides, it was found that the copper oxidation would seriously affect Cu/NC adhesion. The shear test results show that Cu is the best metallization for NC in die-attach joining among the metallizations studied. The fractographic analysis of the substrates reveals that NC/Cu failure mode is bulk failure leading to relatively higher failure strength. The failure modes of Ni-Sn-P/NC, Cr/Ni/Au and ENIG are bulk-partial pad peeling failure.

This work has investigated NC as a solder metallization (NC and Sn-3.5Ag) and NC as a die attach / joining material (NC and different metallizations). Sintered NC will form a porous nanostructure, which causes its morphology and kinetic difference in reacting with Sn-3.5Ag as compared with dense Cu. The interfacial reaction study between NC and Sn-3.5Ag could provide a valuable reference for reaction conditions related to NC and Sn-3.5Ag. NC's adhesion with different metallizations reveals that metallization may not necessary for NC paste on Cu substrate. Both Au finish and Cu surface have shown relatively good adhesion with NC. In order to utilize NC as joining material, removing copper oxide is very critical in forming a strong joint. The joining material application of NC has several advantages that provide it a potential to replace traditional joining materials such as solder, glass frit, conductive and non-conductive adhesives.

5.2 Recommendations for Future Work

Based on the understandings generated by present work, the following work is recommended for further studies:

In the present work, it has been found that NC is a potential solder material in electronic packaging. Solder metallization and die-attach application of NC have been studied in this thesis. Both NC/Sn-3.5Ag study and NC/different metallization study could provide supportive reference for NC's further applications.

Recently, a few researchers are working on applying NC into three-dimensional (3D) packaging. They utilize ink-jet printing to print Cu pillars between different stacked chip layers to form a Through Silicon Via (TSV) structure. Different from conventional TSV processes used in Back End of Line (BEOL) packaging, the ink-jet printed NC pillar have

advantages, such as vacuum-independence, smaller critical dimension and highly controlled morphology[93]. According to the adhesion study in this thesis, it is better to directly join the ink-jet printed Cu pillar with Cu substrate without adding any extra metallizations.

Besides 3D printing application, NC application study could also focus on aerospace soldering. Conventional solders could cause serious Sn whisker problems in aerospace [94]. In order to decrease Sn whisker risks, Pb-Sn solders are used. Pb-Sn layers can lower the stress generation in solder joint, which is the driving force for Sn whisker growth, and therefore, reduce Sn-whisker growth [95]. However, a recently study in NC proves that sintered NC tensile strength is already in the range of space qualified solder, which shows that NC could also be an alternative choice for aerospace soldering. In order to apply NC as a solder material in aerospace application, the mechanical and electrical properties of NC and other solders should be further studied. In my study, NC/Sn-3.5Ag's interfacial reaction is very aggressive. They will form porous Cu_6Sn_5 and these IMCs will elongate rapidly at 230 °C. The mechanical strength and electrical properties of the porous and elongated Cu_6Sn_5 are worth further investigation.

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