NANYANG
TECHNOLOGICAL
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**DEVELOPMENT OF COPPER NANOPARTICLES FOR
LOW TEMPERATURE DIE-ATTACH APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Copper nanoparticles (Cu NPs) that are passivated with thin layers of amine-based organic materials is studied as a low temperature die attach material. Due to the high surface energy of these Cu NPs, they need a protection layer to prevent spontaneous fusion. However, it is important to have these passivation layers removed for effective sintering. Since these layers prevent fusion, the Cu NPs will have high electrical resistance before any thermal sintering. Therefore, a fast and effective technique has been developed based on observation of electrical resistance measurements during sintering of Cu NPs when subjected to different sintering parameters. Based on the change in electrical resistance, a sintering model of the Cu NPs used in this study has been developed. It was observed that the onset temperature of volatilization and onset temperature of fusion are closely related to the final microstructures of the sintered Cu NPs. For good fusion of these Cu NPs, the passivating layers and the organic materials that are present in the Cu NPs paste must be effectively and completely removed. Any presence of passivating materials will hinder the fusion of Cu NPs that leads to low neck growth.

Though it was reported that a higher heating rate is beneficial for the Cu NPs to achieve a denser sintered layer, it is not necessary for the case in this study. If the passivating layers are not removed completely when subjected to higher heating rates, the fusion of the Cu NPs is poor and it will lead to lower shear strength. In addition, based on the electrical resistance measurements, it is observed that when the onset temperature of volatilization is high, it will lead to a higher fusion temperature and the degree of necking between Cu NPs will be high. To leverage on the effect of high heating rates, fast and complete removal of all organic materials within the layer must be carried out. However, this usually would not happen when the heating rate is too fast and/or the peak sintering temperature is $< 200^{\circ}\text{C}$ unless sintering is done under a reactive atmosphere. Therefore, to remove the amine-based passivation layers

faster, formic acid vapor is introduced into the sintering furnace. When formic acid vapor is used, it reacts with the amines-based passivation layers to separate them from the Cu NPs surfaces. Hence the fusion of Cu NPs will occur. Since the reaction is faster than sintering in N₂ ambient, more fusion was observed and the increase in shear strength was significantly higher when formic acid vapor was introduced only at 200°C instead of throughout the sintering process. This again shows that fusion of Cu NPs at 200°C is possible only when the passivation layers are effectively and completely removed. The thermal stability and the level of oxidation of the sintered Cu NPs joint after 1000 hours of isothermal annealing at 150°C in air have demonstrated the potentiality of this material to be used to replace current solder materials.

Lastly, application of Cu NPs paste was demonstrated for high power LEDs and compared directly with commercially available AuSn solder. The electrical, mechanical and optical properties of the LEDs modules bonded with Cu NPs are comparable or even better than those LED modules that were bonded with AuSn solders. Moreover, the peak sintering temperature of Cu NPs is 40°C lower than AuSn reflow temperature. Thus, this material has the potential to lower the overall thermal budget that eventually will reduce the overall manufacturing cost.

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Table of Contents

Abstract	i
Acknowledgements.....	iii
Table of Contents.....	iv
Table Captions.....	viii
Figure Captions.....	ix
Abbreviations.....	xvi
 Chapter 1	 1
Introduction	1
1.1 Problem Statement	2
1.2 Objective and Scope.....	3
1.3 Dissertation Overview	4
1.4 Findings and Outcomes/Originality	6
References	6
 Chapter 2	 8
Literature Review	8
2.1 Overview of interconnects	9
2.1.1 Solder.....	9
2.1.2 Copper Pillar Bumps	12
2.1.3 Electrically Conductive Adhesives (ECAs).....	13
2.1.4 Die attach materials for high temperature applications	14
2.1.4.1 Requirements for High Temperature Die Attach Materials	
13	
2.1.4.2 Metallic Nano-sized Materials.....	15
2.2 Overview of Sintering Nanoparticles	23
2.2.1 Sintering Mechanism.....	23
2.2.2 Challenges of Nanomaterial Sintering.....	26
2.3 Nano Cu Sintering and its Thermal Stability	29
2.3.1 Sintering Temperature	29
2.3.2 Heating Rate.....	29

2.3.3 Sintering Time.....	30
2.3.4 Stability of Cu Joint.....	31
2.4 Sintering Behavior of Cu NPs and Removal of Organic Materials.....	31
2.4.1 Removal of solvent and capping layers	32
2.5 PhD in Context of literature	34
References	35
 Chapter 3	 44
Experimental Methodology	44
3.1 Rationale for Selection of Methods	45
3.2 Post-Processing and Sample Preparation of Cu NPs.....	46
3.2.1 Washing of as-synthesized Cu NPs.....	46
3.2.2 Sample Preparation for Electrical Resistance Studies.....	47
3.2.3 Sample Preparation for Bonding Applications	48
3.3 Characterization of Cu NPs.....	49
3.3.1 Thermal gravimetric analysis (TGA)	49
3.3.2 Differential Scanning Calorimetry (DSC)	51
3.3.3 <i>In-situ</i> electrical resistance measurements.....	52
3.3.4 Shear Test.....	53
3.3.5 Field Emission Scanning Microscopy with Focused Ion Beam Milling Capability.....	55
3.3.6 X-ray diffraction (XRD)	56
3.4 Overview of Methodologies.....	58
References	59
 Chapter 4	 61
Sintering and Densification Behavior of Nano-sized Copper Particles.....	61
4.1 Introduction	62
4.2 Principle Outcomes.....	65
4.2.1 Characterizations of Cu NPs.....	65
4.2.1.1 <i>In-situ</i> Electrical Resistance Measurement.....	66
4.2.1.2 Particle growth and electrical resistance measurements ...	70
4.2.2 Sintering Process of Cu NPs	73

Table of Contents

4.2.2.1 Relationship between T_E and T_F	74
4.2.2.2 Relationship between Heating Rates and Volatilization ...	75
4.2.2.3 Microstructure evolution of Cu NPs at Different Heating Rates	78
4.2.2.4 Further Growth and Densification during Isothermal Annealing.....	80
4.2.2.5 Determining the Dominant Sintering Mechanism	86
4.2.3 Stability of Passivating Ligands under Acidic Environment.....	91
4.3 Conclusion.....	99
References	100
 Chapter 5	 107
Influence of Sintering Parameters on Bond Strength of Cu NPs	107
5.1 Introduction	108
5.2 Experimental Method.....	108
5.2.1 Bonding and characterizations of fused Cu NPs.....	108
Influence of Sintering Parameters on Bond Strength of Cu NPs	109
5.3.1 Effect of Heating Rate	109
5.3.2 Effect of Bonding Temperature.....	114
5.3.3 Effect of Applied Pressure	117
5.3.4 Effect of Bonding Environment	125
5.3.5 Relationship between Microstructure, Porosity and Bond Strength	126
5.4 Bonded Cu NPs stability over time	132
5.4.1 Bond strength	132
5.4.2 Synchrotron μ XRD.....	135
5.4.2.1 Relationship of Shear strength with (111) FWHM.....	137
5.5 Conclusion.....	138
References	140
 Chapter 6	 145
Cu NPs as Interface Materials for High Power LEDs	145
6.1 Introduction	146

Table of Contents

6.2 Experimental Methods	147
6.3 Principle Outcome	147
6.3.1 Overview of Cu NPs as a LEDs die attach material.....	147
6.3.1.1 Mechanical Measurements	149
6.3.1.2 Electrical Measurements	150
6.3.1.3 Optical Measurements.....	153
6.3.1.4 Thermal Resistance Comparison	154
6.3.2 Reliability Tests.....	155
6.3.2.1 Isothermal Ageing.....	156
6.3.2.2 Thermomechanical Reliability.....	162
6.4 Conclusion.....	167
References	167
 Chapter 7	170
Discussion and Future Work	170
7.1 General Discussion	171
7.1.1 Understanding Cu NPs Sintering Mechanism Through <i>In-Situ</i> Electrical Resistance Measurement	171
7.1.2 Enabling Low Temperature Bonding Using Cu NPs	173
7.1.3 Cu NPs Bonding Application in High Power LEDs Die Attach..	174
7.2 Reconnaissance work not included in main chapters	176
7.3 Outstanding Questions	177
References	179
 Appendix	180

Table Captions

Table 2.1 Important Properties of Solder Alloy	10
Table 2.2 Exponents for different sintering mechanisms [48]	20
Table 2.3 Values of m, n and H for Equation 2.3 [68].....	25
Table 5.1 Relative intensity of aged Cu NPs.....	136
Table 6.1 Shear strength of LED modules bonded with Cu NPs and AuSn solder	150
Table 6.2 Electrical resistance of LED modules bonded with Cu NPs and AuSn solder	152
Table 6.3 CTE of materials across the entire LED module [12]	164

Figure Captions

Figure 2.1 Fractured Flip Chip Joint [5]	11
Figure 2.2 Example of squashed bump due to over bonding [20].....	13
Figure 2.3 Schematic diagram and cross-sectioned FESEM of nanowires bonded with Sn-based solder	16
Figure 2.4 Top view of Cu nanowires bundles after removing of the AAO template	17
Figure 2.5 T_m/T_{MB} ratio with particle diameter	19
Figure 2.6 Schematic diagram of the different sintering mechanism for a two- particle model	25
Figure 2.7 Difference between agglomeration and aggregation of nanoparticles during sintering	27
Figure 2.8 Schematic diagram of rate of densification as a function of temperature	28
Figure 3.1 Schematic diagram of the post-processing of Cu nanoparticles before sintering	46
Figure 3.2 Picture of the simple Electrical Test Structures.....	47
Figure 3.3 Schematic diagram of a TGA	50
Figure 3.4 Schematic diagram of a DSC.....	51
Figure 3.5: Shear test setup	53
Figure 3.6 Schematic diagram of the shear test setup.....	55
Figure 3.7 Cross-sectioned SEM image of a sintered Cu NPs layer	56
Figure 3.8 Schematic diagram of Bragg's law [8].....	57
Figure 4.1 TEM image of Cu NPs used (b) Zoomed-in image of a Cu NP (c) Schematic diagram of how the ligands are attached on Cu NPs	64

Figure 4.2 TGA and electrical resistance curves of Cu NPs heated from 25°C to 300°C.....	66
Figure 4.3 FESEM image and schematic illustration of Cu NPs before sintering	67
Figure 4.4 Schematic illustration of the regularly arranged Cu NPs	68
Figure 4.5 FESEM image and schematic illustration of Cu NPs after volatilization and onset of neck growth at 150°C	70
Figure 4.6 FESEM image and schematic illustration of subsequent neck growth of Cu NPs at 300°C when heated at 10°C/min	70
Figure 4.7 Fused Cu NPs sizes as a function of temperature and the corresponding change in electrical resistance.....	72
Figure 4.8 (a) FESEM images of microstructure evolution (Scale 500 nm), and (b) Schematic diagram of the Cu nanoparticles at different stages of sintering	73
Figure 4.9 Heat flow and change in electrical resistance of Cu NPs as a function of temperature	76
Figure 4.10 <i>In situ</i> electrical resistance for Cu nanoparticles heated at different rates to 200°C.....	78
Figure 4.11 Microstructure changes of Cu sintered at (a) 7°C/min (b) 17°C/min (c) 30°C/min (d) 40°C/min (Scale: 500 nm)	80
Figure 4.12 Resistance as a function of isothermal annealing duration for different heating rate samples.....	83
Figure 4.13 Microstructure evolution during isothermal annealing of Cu particles that were previously heated up at different heating rates (Scale bar in white: 500 nm)	86
Figure 4.14 Experimental results and proposed model prediction of resistance as a function of time (a) 7°C/min (b) 17°C/min	87

Figure 4.15 Experimental results and proposed model prediction of resistance as a function of time (a) 30°C/min (b) 40°C/min	89
Figure 4.16 Schematics diagram of Cu NPs microstructure evolution after (a) complete removal, (b) incomplete removal of organic materials.	90
Figure 4.17 XRD of sintered Cu NPs film at 300°C	92
Figure 4.18 <i>in situ</i> electrical resistance measurements during heat up at 40°C/min under N ₂ and formic acid.....	92
Figure 4.19 Changes in T_F when HCOOH vapor is introduced with a heating rate of 40°C/min.....	94
Figure 4.20 Microstructure evolutions of Cu NPs (a) under conventional N ₂ sintering profile (b) under high heating up rate with 18.125M HCOOH vapor (Scale bar: 500 nm)	95
Figure 4.21 Microstructure of Cu NPs sintered under (a) N ₂ (17°C/min) (b) 18.125M Formic Acid Vapor (40°C/min).....	96
Figure 4.22 μ XRD for samples heated under (a) N ₂ (b) Formic acid	97
Figure 4.23 Schematic diagrams showing the sintering behavior under (a) N ₂ and (b) Formic acid	98
Figure 5.1 Schematic diagram of how the passivating layers on the Cu NPs escape under (a) covered and (b) uncovered structure.....	110
Figure 5.2 FESEM images of un-sintered Cu NPs. (a) Top view, (b) Cross sectioned and (c) Zoom in of the bonded layer	111
Figure 5.3 Shear strength of sintered Cu NPs joints at different heating rate	112
Figure 5.4 Microstructure of Cu NPs joint at ramping rate of (a) 7°C/min (b) 17°C/min (c) 30°C/min (d) 40°C/min (Scale Bar: 500 nm).....	113
Figure 5.5 Microstructures evolution of Cu NPs bonded at (a) 200°C (b) 250°C (c) 300°C for 0 – 20 min (scale bar: 1 μ m)	116

Figure 5.6 Shear Strength as a function of isothermal duration at 200°C, 250°C and 300°C	117
Figure 5.7 Porosity of Cu NPs layer with respect to time for samples bonded at 200°C, 250°C and 300°C.....	117
Figure 5.8 Schematic diagram of bonding without and with bonding pressure exerted	119
Figure 5.9 Schematic diagram of deformation between Cu NPs	121
Figure 5.10 Relationship between shear strength and porosity as a function of bonding pressure	124
Figure 5.11 FESEM images of fracture surfaces and cross sectioned of sintered Cu joints at (a) 0 MPa (b) 1 MPa (c) 3 MPa (d) 5 MPa (Scale bar of 500 nm)	125
Figure 5.12 Cross-sectioned FESEM images of sintered Cu with and without pressure.....	126
Figure 5.13 Shear Strength of Cu NPs joint under N ₂ and Formic Acid	127
Figure 5.14 Microstructures of the sintered Cu NPs under (a) N ₂ and (b) formic acid vapor	128
Figure 5.15 <i>in-situ</i> Electrical resistance measurements under N ₂ and formic acid vapor environment.....	129
Figure 5.16 Schematics illustration of densification at (a) 200°C and (b) 300°C (Scale bar: 1 µm).....	131
Figure 5.17 Failure types and locations (a) Type 1: Propagate along weakly bonded Cu NPs (b) Type 2: Does not propagate easily along Cu NPs due to strong bonding	132
Figure 5.18 Shear strength of sintered Cu NPs under isothermal ageing at 150°C for 1000 hours	133

Figure 5.19 Microstructure evolutions of bonded Cu layers during ageing test from 0 — 1000 hours (Scale bar: 500 nm)	135
Figure 5.20 XRD patterns of Cu NPs (a) before (b) after ageing for 1000 hours	137
Figure 5.21 Graph of shear strength and line width (FWHM) as a function of ageing time.....	139
Figure 6.1 As-reflow single-chip LED module	148
Figure 6.2(a) Overview of the LED module bonded with (a) Cu NPs paste with (b) Zoom-in view of the bonded layer; (c) AuSn solder with (d) Zoom-in view of the bonded layer (scale 10 μ m).....	149
Figure 6.3 FESEM cross-sectioned image of Cu NPs on the LED die after shear test	151
Figure 6.4 Schematic diagram of the electrical resistance measurement setup of LED module.....	152
Figure 6.5 Photoluminescence spectra of Cu NPs and AuSn die-attach LEDs operated at 3 V at room temperature.....	153
Figure 6.6 Measured temperature with time for Cu NPs and AuSn LED samples	155
Figure 6.7 Shear Strength of Cu NPs LED die after 1000 hrs of thermal aging	156
Figure 6.8 Microstructural changes of Cu NPs bonded onto LED.....	158
Figure 6.9 Microstructures of Cu NPs (a) just after sintering, (b) after 1000 hours at 200°C	158
Figure 6.10 Fracture surfaces of LED dice and substrate after (a) 250 hours (30 μ m scale) (b) 1000 hours of isothermal ageing at 200°C (100 μ m scale).....	159
Figure 6.11 Schematic diagram of crack propagation through Cu NP layer .	159

Figure 6.12 Electrical resistance of Cu NPs with Au LED from 0 – 1000 hrs of isothermal ageing test.....	161
Figure 6.13 Photoluminescence spectra of Cu NPs on Au metallization of a white light LED (blue + phosphor) operated at 3 V at room temperature for different ageing period	162
Figure 6.14 Shear strengths of Cu NPs bonded LEDs after thermal cycling.	163
Figure 6.15 FESEM images of Cu NPs LED modules after (a) 100 cycles, (b) 200 cycles, (c) 300 cycles (Scale: 20 μ m).....	164
Figure 6.16 Voids were present at the bonding interface between Cu NPs and (a) Ag, and (b) Au metallization after sintering.....	166
Figure 6.17 (a) FESEM image of sheared surface of an as-bonded LED chip (b) Zoomed-in on the “islands” of sintered Cu NPs clusters.....	166
Figure 7.1 Color change during bonding under (a) N ₂ (b) Formic Acid.....	176

Abbreviations

DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction

Chapter 1

Introduction

Die attach materials are used as a bonding material between a die and a substrate. They play a key role in the performance and reliability of the overall microelectronics package. Some of the common die attach materials are gold alloys, solders and polymeric adhesive pastes or films. Recently, the development of gallium nitride (GaN) and silicon carbide (SiC) for high power electronics in automotive, aerospace, high-brightness light-emitting diodes (HBLEDs) and sensor technology has led to a surge in the demand for lead-free soldering material that is able to meet the high temperature electronics requirements. Hence, several new die attach materials are in development. Among them are the metallic nanoparticles (NPs) such as Au, Ag and Cu that have gained tremendous interest in this field. This is attributed to its high electrical and thermal conductivity, low elastic modulus that enables good thermo-mechanical reliability, its ability to be processed at lower temperatures due to their high surface energies and yet able to operate at high temperatures. However, though the metallic nanomaterials found in literatures are similar, the synthesis technique, the size and size distribution of NPs, and the capping layers are very much different. Hence, this thesis will investigate the feasibility of a chemically synthesized Cu NPs to be used as a die attach material in high power electronics, and at the same time develop ways to study such materials in general.

1.1 Problem Statement

High-power semiconductor devices currently represent one of the highest growth sectors of any semiconductor technology, with many key applications including motor control, high-brightness light-emitting diodes (HBLEDs), solar concentrator cells, and radio-frequency (RF) and microwave circuits used in radar and telecommunications equipment. From a packaging perspective, there are a number of common requirements for all these high-power applications. They must be able to handle high electrical currents, possess a higher melting point than the operating temperature, able to dissipate large amounts of heat, manage thermal expansion-induced stresses for high reliability, and this must all be accomplished at low cost. The problem with current conventional soldering materials, such as Tin-Silver-Copper (SAC), is that it has a low working temperature as it melts at a low eutectic temperature of 217 °C. Therefore, they are not suitable as the SiC power transistor die attach because the melting temperature of the solder is much lower than the potential application temperature of >250°C [1]. Thus, lead-tin (PbSn) solder, typically Pb90Sn10 which has a liquidus temperature of 302°C, is still commonly used for power semiconductors. Another advantage of this material is its high ductility and acceptable thermal conductivity. However, due to its high Pb content, it has negative effects on health and the environment. To overcome this problem, AuSn or AuSi solders are the best alternatives. Both types of solders have high melting temperatures, good thermal and electrical conductivities. However, the major drawback for both of these materials is their cost. In addition, when compared with other low temperature solders, AuSn and AuSi have lower ductility and require a higher die attach temperature, making thermal coefficient of expansion (TCE) stress an issue. When AuSn solders are used on Cu lines, the formation of irregularly (Au, Ni) Sn intermetallic on Cu lines can lead to lower mechanical strength.

With all these problems stated above, it is important to develop and understand the next alternative material to be used in interconnects and die attach material technology, especially for high power electronics applications. This new material must be able to process at low temperature ($\leq 200^{\circ}\text{C}$), has a high melting point after processing ($>300^{\circ}\text{C}$), good mechanical strength, high electrical and

thermal conductivities. The compatibility, i.e. good wetting and little or no intermetallic formation, with common metallization such as copper, silver, gold or nickel is necessary. In addition, it must not be too expensive and be able to be integrated into the current processing system with minimum or no changes required. It is well-known that nanoparticles have a higher surface energy than bulk form due to its higher surface area to volume ratio. As a result, metallic nanoparticles can be fused at a much lower temperature. Therefore, if copper nanoparticles can be used as a paste similar to the solder paste currently adopted in the die attach technology, it can have the excellent properties of a bulk copper such as high electrical and thermal conductivities after reflow (i.e. sintering), yet maintain a low processing temperature as that used currently in the solder reflow process. Furthermore, with Cu NPs as a die attach material, it can potentially improve the joint's bond strength as no IMCs would be formed within the joint that would lower the bond strength. Hence reliability can be improved as compared to current solder materials.

1.2 Objective and Scope

The objective of this study is to understand a new lead-free nanomaterial for die attach technology by studying the processing-microstructure-property relationship, which is the low temperature sintering of copper nanoparticles paste. The scope of this project will cover the processing procedure of the as-synthesized copper nanoparticles paste to suit the current surface mount technologies such as syringe-dispensing and screen/stencil-printing. Detailed study on its physical sintering mechanism such as removal of organic materials, fusion and densification of the nanoparticles at different processing parameters will be carried out. Microstructure evolutions with various changes in sintering parameters and long-term joint stability after sintering will also be studied. Finally, the feasibility of adopting this material as a die attach material for commercially available LEDs dies and substrate will be studied and benchmarked against the high temperature AuSn solder. The mechanical, electrical and optical properties of the sintered Cu NPs joints will be analyzed through the bonded joint. Lastly, reliability testing such as thermal ageing and thermal cycling will also be done to understand the potential failure mechanisms.

1.3 Dissertation Overview

This thesis addresses the issues and challenges of today's materials used in the interconnect and die attach technology. In addition, this thesis also investigates and discusses about a new viable material, copper nanoparticles paste, that can be used in the current and future interconnect and die attach technology.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the types of interconnect and die attach technology and their limitations and challenges towards current and future electronics devices. The development of future interconnects and die attach materials such as copper pillars, copper pillar bumps and metallic nanoparticles to be used as the next solder materials, will be discussed. With the introduction of Cu pillar and Cu pillar bumps, it does help to solve certain issues such as stand-off height and shorting between solder bumps due to smaller pitch. However, high processing temperature in the previous and formation of intermetallic in the latter pose some challenges for them to be adopted. Hence the development of metallic nanoparticles paste comes into the picture. These metallic nanoparticles are able to form connecting paths based on the principle of sintering that has been very well developed, especially for ceramics materials. However, due to its small diameter, it has a high surface energy that enables these metallic nanoparticles to be sintered at low temperature. Till date, there are not much studies on Cu nanoparticles. One of the reasons being its tendency to oxidize easily that affects its electrical properties. Hence this chapter will also be looking into the current studies on Cu nanoparticles and areas that have yet to be studied but worth the attention.

Chapter 3 discusses the experimental methodology used in this entire study. First, the post-processing procedures of the synthesized Cu nanoparticles needed to be carried out to suit specific applications are explained. Some of the characterization techniques used to study the thermal properties of copper nanoparticles before sintering includes thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Microstructures evolution based on changes in electrical resistance during sintering are studied in detail using Field-Effect Scanning Electron Microscopy (FESEM) coupled with Focused-Ion

Beam (FIB) milling capability. Energy dispersive X-ray spectroscopy (EDX) was also used to study the chemical and elemental analysis of the sintered and aged copper joint.

Chapter 4 discusses about the sintering and densification behavior of nano-sized copper particles. TGA, DSC and *in-situ* electrical resistance measurements during sintering were used to study the thermal, physical and electrical changes that arose under the different processing parameters. It is observed that the heating up rate has a direct influence on the onset temperature of evaporation of organic materials (T_E), which subsequently affects the fusing temperature (T_F). Moreover, the rate of evaporation of organic materials under different environment such as inert and formic acid vapor, has an impact on the rate and uniformity of passivating layers' removal on the Cu NPs. These changes in process parameters and environment will eventually affect T_E and T_F , electrical resistance and microstructure such as size and amount of porosities of the sintered Cu layer. The microstructure at different stages of sintering under different process parameters and environment were captured with the help of the *in-situ* electrical resistance measurements. Hence this chapter will provide an in-depth study on the relationship between process parameters and final microstructure of sintered Cu NPs.

Chapter 5 discusses about the relationship between sintering parameters and the resultant microstructure of the Cu NPs that is used as a die attach material. As this study is targeted towards the bonding application, mechanical properties such as the shear strength of the bonded joints are tested and related with the amount of porosities and degree of necking between fused Cu NPs clusters. Since the removal of capping layer is critical for good fusion of Cu NPs, the capability to remove and the impact of fast and effective removal of these capping layers on the resultant microstructure and shear strength are presented and further discussed. Two different failure modes that led to a good or poor joint strength are outlined based on the type of microstructures that have resulted from the different sintering parameters. The effect of long term thermal stability of the sintered joints were also carried out to further understand the microstructure evolution, grain growth and degree of oxidation with its final mechanical shear strength.

Chapter 6 discusses the feasibility of adopting such Cu NPs paste for high power LEDs applications. Commercially available high temperature solder, AuSn, was used as a comparison. From the initial bonding, the Cu NPs demonstrated a comparable or better performance than AuSn solder in terms of mechanical, electrical and optical properties. This is attributed to the good physical properties of Cu, the lack of formation of IMCs or “big voids or cracks between Cu NPs and bonding interfaces”. To understand the long term reliability of such material, long-term high temperature storage test at 200°C for 1000 hours and thermos-mechanical test were carried to understand the reliability of this novel material on actual LED modules.

Chapter 7 gives an overall discussion with three sub sections that give a summary of the findings and implications for the three main findings of this study. It also addresses and discusses on the results achieved with the initial designed target that was eventually met. Some questions were raised during the course of study and future works are being proposed.

1.4 Findings and Outcomes/Originality

This research has led to several novel outcomes by:

1. Establishing a simple and quick technique to monitor the onset temperature of evaporation and fusion of NPs capped with organic materials. Such information is important for developing a good sintering profile for different NPs paste formulations for different applications. This technique enables the study of the initial dominating sintering mechanism of NPs by relating the changes in electrical resistance with time.
2. Understanding the relationship between the rates of change in electrical resistance, the onset temperature of evaporation and fusion with the resultant microstructures. The strength of the sintered joints, which is closely related to the microstructure, can thus be improved.
3. Providing an insight into the feasibility and reliability of such novel material as a die attach material for high power LEDs applications.

References

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Chapter 2

Literature Review

In this chapter, electronic packaging materials such as solder, copper pillar bumps and metallic nanoparticles will be reviewed. However, the focus will be on metallic nanoparticles, specifically the influence of process parameters on its sintering behavior. As nanoparticles faces a different set of challenges due to its high surface to volume ratio, the sintering mechanism of these nanoparticles and the challenges will be very different from bulk and thin film. Another topic that is considered is the removal of capping layers on these metallic nanoparticles. Such capping layers are a barrier to successful fusion of nanoparticles that will cause reliability issues if the removal is not complete. Moreover, the type of capping layers used and the type of by-products it produces can also affect the sintering temperature of the nanoparticles as the sintering temperature is heavily dependent on the decomposition or volatilization temperature and presence of such organic materials can hinder fusion of nanoparticles. To further study the feasibility of replacing current solder with these low processing temperatures metallic nanoparticles, the influence of different sintering parameters such as temperature, time and heating rate with its thermal stability are being discussed as well. Such thermal stability is particularly important for high or harsh environment applications. With these background knowledge, this thesis will focus on to develop and study on low temperature bonding process (~200°C) using copper nanoparticles for robust interconnection and die attach applications

2.1 Overview of interconnects

In conventional technology for interconnecting electronics devices, it typically involves die-attaching one terminal of the semiconductor die to a heat-sinking substrate with solder alloys or conductive epoxies and wire-bonding fine aluminum or gold wires to the other terminal(s). This joint layer, which is typically referred to as the bond-line, acts as an electrical connection, a mechanical bond and a heat transfer medium. Therefore, the quality of this bond-line in the chip attachment is very important to the overall performance and reliability of the electronic package.

As technology progresses, the drive to reduce the fabrication cost and energy conservation consumption has put an increasing pressure on the energy density within the power modules. This means that more chips must be placed into a single package. Hence, there has been a growing trend for flip chip interconnection using micro bumps with reducing pitch as the electronics industry moves towards high density and better performance devices. However, with fine-pitch solder bumps, it brings about several challenges and issues in terms of packaging assembly process and reliability performance [1]. Currently, there are three major types of chip attachment materials/techniques. They are solder reflow, Cu pillar and/or bumps, electrically conductive adhesive (ECAs) and some low temperature joining techniques that uses nanoparticles or nanowires. All these three materials would be reviewed subsequently.

2.1.1 Solder

The use of solder alloys as metal joint materials can be dated back to thousands of years. With the development of modern electronic packaging technology, solder alloy is used as an interconnecting material in electronic packaging as solder joints to provide both the electrical connection and mechanical support in electronic packaging modules [2]. The melting point of solder and its ability to self-align make it valuable in the microelectronics industry [3]. Since Pb-Sn solders have been acknowledged to be harmful to men's life and environment, new solders alloys are being looked into. When trying to identify alternatives to the Pb-Sn solders, it is important to ensure that the properties of the replacement

solder are either similar to or superior than Pb-Sn solders. Table 2.1 summarizes the important properties that a solder alloy should possess [4].

Table 2.1 Important Properties of Solder Alloy

Properties relevant to manufacturing	Properties relevant to reliability and performance
Melting/liquidus temperature	Electrical conductivity
Wettability	Thermal conductivity
Cost	Coefficient of thermal expansion
Environmental friendliness	Shear properties
Availability and number of suppliers	Tensile properties
Manufacturability using current processes	Creep properties
Ability to be made into balls	Fatigue properties
Copper pick-up rate	Corrosion and oxidation resistance
Recyclability	Intermetallic compound formation
Ability to be made into paste	

Though some lead-free solders can meet the regulation and properties requirements stated in Table 2.1, they are either high in price (Au80Sn20, Au97Si3, Au88Ge12) or hard to process (Zn95Al5). Hence to date, most lead-free solders that are more economical are mostly Sn-based. The commonly used is the eutectic alloys of Sn and noble metals of Au, Ag and Cu [5]. With regards to the microstructures of these Sn-noble metal eutectic solders, they consist of a mixture of Sn and intermetallic compounds (IMCs). Hence the mechanical properties of these eutectic solders will be anisotropic when the dispersion of the IMC is inhomogeneous [5]. In addition, with the formation of such IMCs, it could attribute to the formation of high stress region between solder bump and under-bump-metallization (UBM). Cracks are most likely to be initiated and will propagate along such interface leading to failure as shown in Figure 2.1.

Figure 2.1 Fractured Flip Chip Joint [5]

The most commonly used lead-free solder, SAC (Tin-Silver-Copper), has a significantly higher melting point of $\sim 217^{\circ}\text{C}$ than traditional Sn/Pb solders (183°C for 63/37 Sn/Pb and 188°C for 60/40 Sn/Pb), thus limiting the choice of substrates used for processing as well as requiring a higher thermal budget. Moreover, with the high Sn content in SAC solder, tin whisker formation can lead to electrical shorting [6, 7]. In addition, traditional solders are becoming more restrictive as the interconnect size continues to shrink to meet the input/output (I/O) demands of high performance components [8]. The International Technology Roadmap for Semiconductors (ITRS) has forecasted that the minimum pitch for area array interconnects to shrink to $120\text{ }\mu\text{m}$, $100\text{ }\mu\text{m}$, and $85\text{ }\mu\text{m}$, in 2010, 2015, and 2020, respectively [9]. In the past, solder joints in flip-chip microelectronic packages have their diameters in the $100\text{ }\mu\text{m}$ range. However, in today's development of the three-dimensional integrated circuits (3D ICs), the diameter of a typical micro-solder joint is merely about $10\text{ }\mu\text{m}$. With such transition from flip-chip to 3D ICs, the volume of the solder joint has shrunk tremendously. Many new issues will arise due to the reduction of the solder volume and stand-off height (SOH). This will eventually affect the reliability of the solder joints [10-12]. The low standoff height is of concern from mechanical fatigue life point of view because of the higher shear after assembly and void trapping during the underfill process [13].

Meanwhile, miniaturization of the solder volume could cause the entire solder layer to completely transform into intermetallic compounds (IMCs) during the device operation, or even after its fabrication. As IMCs tend to be hard and brittle, a solder joint composed entirely of IMCs would have poorer mechanical properties [10, 11, 14, 15].

For mechanical reliability issues, most solder joint failures fall under three major categories: 1) tensile fracture due to stress overloading, which is short-term; 2) creep failure due to the application of a long-term, permanent load; and 3) fatigue failure due to the application of cyclical stresses. More than one of these stresses can act on a solder joint in a given situation, so solder joint failure analysis can be challenging at times [4].

2.1.2 Copper Pillar Bumps

Cu pillar bumps are an interesting alternative to conventional solder bumps for first-level flip chip interconnections. Pillar bump is a novel interconnects structure, including a non-reflowable base and a reflowable cap like a pillar shape [16]. They offer benefits like finer pad pitch without sacrificing standoff, significantly higher current carrying capability and better thermal performance and resistance to electromigration [17-19]. Moreover, the solder cap does not wet the copper pillar sides thus allowing the benefit of more space for underfill flow which improves the reliability performance of copper pillars [18]. Another issue faced by conventional solder is bump bridging. However, such problem can be alleviated by using Cu pillar bumps which are designed to have thick Cu UBMs and thin solder layers for fine-pitch applications. In these cases, the Cu pillar bumps do not experience bump bridging because only small amounts of solder are used. Also, these bumps provide high mechanical strength, because thick Cu pillars allow them to maintain large standoff height between chip and substrate. These advantages will enable Cu pillar bumps to be adopted in fine-pitch applications, such as 3D system-in-package.

However, controlling the formation of brittle intermetallic compounds (IMCs) and weak interfaces during reflow or any heat-related process, and preventing copper migration during bonding and reliability testing remain challenges that

the electronic packaging industry faces [19]. In addition, solder shorts might occur in an over-bonded Cu pillar die as shown in Figure 2.2 where the solder cap can be squeezed out to the sides of the joint [20]. Though the addition of solder cap had avoided the high temperature copper-to-copper bonding step, electrical and mechanical limitations of solder still exist [3].

Figure 2.2 Example of squashed bump due to over bonding [20]

Therefore, the reliability of Cu pillar bumps has become increasingly important. However, at the interface between Cu and solder, Cu_6Sn_5 , Cu_3Sn and Kirkendall voids are usually formed. Formation of IMCs and Kirkendall voids are detrimental to the reliability of flip-chip bonding because IMCs are brittle and possess higher electrical and thermal resistivity than either Cu or solder alloy.

2.1.3 Electrically Conductive Adhesives (ECAs)

Another possible type of die-attached materials is known as the electrically conductive adhesives (ECAs). Such conductive adhesives have been around for a long time and basically they are made up of highly conductive metallic powder that dispersed in a polymer-based matrix. The polymeric resin can be epoxy-based, silicone, or a polyimide and the metallic powder can be silver, gold, nickel or copper [21]. The conductivity of such material is dependent on percolated network formed by the conductive particles. The advantages of ECAs as

compared to conventional solder materials is that it is more environmental friendly, it requires lower processing temperatures thus lower stress on the substrates and its ability to be used for fine pitch interconnects due to the small metallic powder present within the matrix. Therefore, solder are being replaced by ECAs in liquid crystal display (LCD), flip-chip assembly, chip scale package (CSP) and ball grid array (BGA) applications [21-23].

Though ECA offers many advantages such as lower stresses due to low Young's modulus, low processing temperature and relatively lower in cost compared to conventional solder technology, poorer electrical properties which are caused by poor fusion among metallic powder suffer and polymer degradation during high temperature humidity ageing is a major disadvantage [24]. Therefore, such material is not suitable for high-power applications. Therefore the following sections will look into other alternatives which are able to maintain good joint integrity under high temperature application yet economical and has low processing temperature.

2.1.4 Die attach materials for high temperature applications

In today's electronics devices, the demand for high power density and high temperature capability have increased tremendously. With the technologies advancing into SiC-based substrate and other high bandgap materials, it will improve many current limitations that are associated with Si-based technologies. This includes increasing the switching speed, power density and junction temperature [25, 26]. These devices are largely needed in the aerospace, automotive and sensor technology that needs to have its performance maintained at extreme temperature conditions. Therefore, these new die-attach materials that are to be used in these devices must be able to withstand, cope and function suitably under extreme environment to maintain the reliability of the package's die to substrate interconnection.

2.1.4.1 Requirements for High Temperature Die Attach Materials

Usually the main heat dissipation path for high power semiconductor packaging is from the device through the die-attach material. Hence, the die attach layer's thermal characteristics are very important. These characteristics include thermal

conductivity, thermal resistance at interfaces between the die attach, the device and the package, and the thickness of the die-attach layer. Another important property of the die-attach is its electrical conductivity. This is because the electrical resistance between package and die results in joule heating which is an energy-loss mechanism [27]. This is generally influenced by the electrical properties of the die-attach material itself that causes a reduction in energy efficiency of the entire device. In addition, the die-attach layer is also the mechanical interface between the die and the packaging material. If the coefficients of thermal expansion difference across the die, die-attach material and package are huge, certain parts of the die can go into tension and results in die cracking. Besides all the mentioned thermal and electrical properties, another important factor to consider is the cost. Cost consists of the raw materials cost and assembly cost, which is dependent on manufacturing throughput and yields. Other general requirements include the capability to resist corrosion, have good ductility, solidus points of $\geq 260^{\circ}\text{C}$, liquidus point of $\geq 400^{\circ}\text{C}$, thermal shock reliability, good thermo-mechanical fatigue resistance, high thermal conductivity, compliant CTE mismatch between die and substrate and electrical volume [26, 28].

Currently, there are a few commonly used high temperature Au-based solders. They are namely AuSn, AuGe and AuSi. Though they possess high thermal capability and high electrical conductivity, they are very expensive due to the larger portion of gold content. In addition, AuSn, AuGe and AuSi have low ductility, making CTE mismatch a problem, particularly when one considers the high die-attach temperature. Therefore, the common high temperature solder is still $\text{Pb}_{90}\text{Sn}_{10}$. Due to the ductile nature of $\text{Pb}_{90}\text{Sn}_{10}$, it minimizes CTE mismatch between die and substrate. This made the bonding of very large die possible without the risk of cracking. In addition, it has about 80% of the thermal conductivity of AuSn but costs 100 times cheaper. The only drawback of this material is the health risk it brings about. Therefore, a new lead-free alternative with good thermal, electrical conductivity, good ductility and reasonable cost is needed.

2.1.4.2 Metallic Nano-sized Materials

Metallic nanoparticles and nanowires are becoming one of the possible alternatives that are gaining increasing research interest in recent years due to its ability to be processed at lower temperature and ultimately reducing the thermal stress [29]. The low processing temperature as reported by many is similar to that of the current high-lead solder processing temperature [30-32]. In addition, high thermal stability and conductivity, good mechanical and electrical properties as compared to the other lead-free solder substitutes available in the market are some of its advantages. Therefore, many research groups have been actively developing metallic nano-sized materials, Ag or Cu, as the next possible lead-free die-attached materials used in electronics devices [30, 33-35]. Besides being a potential substitute for solder materials due to its ability to process at a lower processing temperature, it too has gained some attention in the flexible electronics sector as the organic substrates used in flexible electronics usually need to be processed at a lower temperature.

2.1.4.2.1 Nanowires/ Nano-solder

Nanowires is a 1D nanostructure that has been widely studied due to its potential to be used as a basic electronic circuit element or be assembled and integrated into functional structures [36]. There are various methods to fabricate such nanowires. One of the most common methods is electrodeposition of the desired material using a nano-porous template as this method is not time-consuming, inexpensive and the growth rate is high. [29, 37, 38]. These templates are usually made of alumina or polycarbonbonate. The template is subsequently removed and the nanowires are released. Good ohmic contacts between these nanowires can be made by using solder materials, usually tin-based, between two nanowires, direct nanowires-nanowires contact or metallic nanowires and metallic micropad as shown schematically in Figure 2.3 [39, 40].

Figure 2.3 Schematic diagram and cross-sectioned FESEM of nanowires bonded with Sn-based solder

However, these 2 techniques do have its challenges. For those nanowires that contain nanosolders, though it can be reflowed under conventional method, addition steps have to be incorporated to include the solder materials on the nanowires. Moreover, the reflow of these tin-based nanosolders can be a complex issue when reactive surfaces such as Cu, Au or Ni are used since they would react and form IMCs. As for direct nanowires-nanowires contact, the formation of oxide on these nanowires can hinder fusion between them and affect the electrical properties [41, 42]. In addition, due to the nanowires template fabrication technique, these nanowires could contain clustering that are more difficult to disperse uniformly as shown in Figure 2.4 [43].

Figure 2.4 Top view of Cu nanowires clustering after removal of the AAO template

Another method of adopting metallic nanowires for 3D interconnect is fabricating nanowires directly onto the template that are created on the substrate [44]. Though this method allows all nanowires to be well-dispersed and vertically standing on the substrate, it could possess some challenges when come to fabrication of nanoporous template for bigger substrates. Non-uniform pores can result and this is undesirable as it can affect the quality of the nanowires fabricated. In addition, oxidation of the standing NW array could result due to nanoscale Kirkendall effect that can affect the fusion temperature, electrical and mechanical properties [42]. Such rapid rate of oxidation could be due to the high aspect ratio of the nanowires. It is observed and explained by Gao *et al.* [41] that the oxidation on nanorod as compared to nanowires can be removed easily during reflow process. This is because when the reflow temperature goes beyond the melting point of the nanorod, the internal pressure of the liquidus nanorod core increases and the outer oxide shell will rupture due to higher tension experienced and this is observed in nanorod as its oxide shell suffers a higher tension as compared to those oxide shell of the high aspect ratio nanowires. Since these nanorods have demonstrated a better removal of oxides and have a depressed melting temperature due to its size and lower aspect ratio, those zero-dimensional nanoparticles shall be considered.

2.1.4.2.2 Metallic Nanoparticles (MNPs)

Printable inks and solder materials which comprise of a certain amount of MNPs has been developed in recent years [45, 46]. It is reported that due to the high surface energy of NPs, the melting point for most elements NPs, with a certain particle size range, reduces almost linearly with the inverse of its radius [47]. The theoretical size-dependent melting point of a material can be calculated through classical thermodynamic analysis using Gibbs-Thomson equation that relates melting temperature with particle size [48].

$$Tm(d) = T_{MB} \left(1 - \frac{4}{\sigma_{sl} H_f \rho_s d} \right)$$

(2.1)

Where: T_{MB} = bulk melting temperature

σ_{sl} = solid–liquid interface energy

H_f = bulk heat of fusion

ρ_s = density of solid

d = particle diameter

Based on this equation, the relationship between melting temperature for a metal particle with its diameter can be graphically represented based on the normalized Gibbs-Thomson equation. This is represented in Figure 2.5 for gold [48].

Figure 2.5 T_m/T_{MB} ratio with particle diameter [48]

Furthermore, Herring's scaling law [49] predicts the sintering time required to get the same degree of sintering by the same sintering mechanism of powder which is geometrically similar and sintered under the same temperature. For the sintering of two kinds of powders with radii a_1 and a_2 and are related by an equation $a_2 = \lambda a_1$, the relationship can be expressed as:

$$\Delta t_2 = \lambda^\alpha \Delta t_1 \quad (2.2)$$

where α is the exponent for the different sintering mechanisms stated in Table 2.1 while Δt_1 is the time required to produce a change in particle 1 and Δt_2 is the time required to produce a geometrically similar change with respect to particle

1 in particle 2. The equation means that the time required to sinter a smaller particle will be shorter.

Table 2.2 Exponents for different sintering mechanisms [49]

Sintering Mechanism	Exponent α
Viscous flow	1
Evaporation and condensation	2
Volume diffusion	3
Surface Migration	4

However, there are a few limitations to Herring's scaling law. First, it assumes only one sintering mechanism is taking place. Secondly, the shape of the particles must be uniform throughout the process. Lastly, the particle size ratio, λ is taken to be constant. For nanoparticles, they tend to agglomerate easily and that can potentially induce unpredicted grain coarsening that leads to a change of the particle ratio.

From Figure 2.5, it can be observed that melting temperature is significantly lower than its bulk when the particle diameter is less than 10 nm. Hence to lower the sintering temperature significantly, the diameter of the nanoparticles should be sufficiently small. The cut-off particle size will differ across different materials as mathematically represented in equation (2.1). If particles are bigger than 50 nm, in the case of gold, its melting temperature will be similar with the bulk. Thus, for such larger nanoparticles, the ability to sinter at a much lower temperature as compared to bulk is therefore not attributed to melting, but the high surface energy that caused sintering through diffusion.

An organic passivating material is required to cap these nanoparticles to prevent unwanted fusion and oxidation prior to sintering. Upon sintering, these organic materials will be detached and/or decomposed from the metallic NPs surfaces and these metallic nanoparticles will fuse to form a conductive network. Although low temperature sintering behavior of Ag NPs has been studied extensively [33, 35], few have reported on Cu NPs [30, 50]. Low temperature sintering of noble metal NPs for die attach is promising since they rely on the principle of atomic diffusion and consolidation rather than a change of state from

solidus to liquidus [26]. In addition, NPs sintering does not need high pressure as compared to micrometer scale powder, as these NPs have much higher surface energy [26]. In Bai *et al.* [33] work, they made a comparison between Ag NPs and Au80Sn20 solder. They reported that the previous has a much lower calculated elastic modulus, i.e. 9 GPa, due to the presence of micro-pores in the sintered Ag NPs. This is an advantage over conventional high temperature solder as it can withstand the stress arising from thermal expansion mismatch during bonding. Though sintered Ag NPs has 2.4 times higher electrical resistivity than bulk Ag at room temperature, its electrical resistivity is still lower than current solder alloy due to presence of pores of these sintered Ag NPs [26]. Hence, factors influencing the final density of the sintered metallic NPs layer such as pressure, sintering temperature, particles size and removal of passivating layers should be considered.

When bonding, pressure is concerned, it is observed that as compared to micron-sized Ag particles, these Ag NPs can be sintered at a much lower pressure i.e. 1 – 5 MPa while keeping the same sintering temperature [32, 35]. This pressure range is much lower than the 9 – 40 MPa range as reported in micron-sized Ag particles sintering [51]. This decrease in sintering pressure is attributed to the higher surface energies due to the smaller size of the NPs.

However, Ag NPs often incurred higher cost and are susceptible to ion migration [52]. When Ag is used as a die-attach, with die pad as anode and a cathodic electrode nearby, the Ag metal can undergo dissolution, creating Ag⁺ ions in the presence of moisture and ionic contaminants. The Ag⁺ ions can then migrate to the cathode since the moisture presence will act as an electrolyte. These Ag⁺ ions will then be reduced at the cathode and pure Ag will build up eventually. Such build-up will lead to dendrites formation that could potentially cause shorts between different interconnects and dies. This is especially so for printed interconnects. Hence the next alternative is to look into Cu NPs sintering as Cu also possesses high conductivity and has strong durability towards ion migration and it is lower in cost as compared to Ag and Au [30, 52].

2.1.4.2.3 Copper Nanoparticles (Cu NPs)

Copper (Cu), with the absence of intermetallic compounds and precipitates formed on the Cu bonding pads, makes it a simpler material than common Sn-based solder. Since Cu is already commonly used in microelectronics technology as trace, interconnect and pad material, it will minimize compatibility issues when adopted. Its ability to operate under high temperature, good electrical and thermal properties is indeed attractive for the next generation of solder alternative. However, to achieve a low processing temperature that is similar to Pb-based solder, a reduction in the particles size is needed. Hence the development of Cu NPs is recently being studied extensively [34, 53, 54]. It is known that Cu oxidizes easily in air which will reduce the electrical conductivity. Thus, these Cu NPs are usually passivated with organic materials to prevent oxidation, and fusion between particles before sintering. To enable low temperature sintering, these passivating layers should be easily removed upon heat treatment ($\leq 200^{\circ}\text{C}$). Since these passivated Cu NPs are not connected with one another, they thus behave like an insulator prior to sintering [55, 56]. Apart from being passivated with layers of organic materials, organic additives are added into the Cu NPs paste. Such additives help to adjust the viscosity of the paste for the ease of dispensing through micron-sized aperture suitable for die-attach materials. These additives and passivating layers are usually made up of alcohol, thiol, amines or acid-based materials [57-60]. With these organic materials, they do affect the overall electrical resistance of the Cu NPs paste matrix [48]. Hence to achieve the desired electrical and mechanical properties of these Cu NPs, these organic materials must be removed from the Cu NPs matrix during thermal treatment to allow subsequent fusion among Cu NPs [48, 61, 62]. Since the removal of the passivating layers affects fusion of these metallic NPs, a fast technique should be developed for the removal of passivating layers and establish its co-relation with the final microstructures that determine the mechanical, electrical and thermal properties of the sintered layer.

2.2 Overview of Sintering Nanoparticles

For many years, soldering technology has been commonly used in die bonding. However, some of the solders (SAC) cannot fulfil the reliability requirements of future power electronics devices whereas some solders are expensive (AuSn, AuSi) or toxic (PbSn) to be used. Hence, the sintering of metallic nanoparticles has been explored in recent years. This technique is promising as these nanoparticles can be sintered at low temperature with little or no pressure exerted due to their high surface energy and its ability to produce thermally and electrically conductive and highly reliable bonds after being sintered [35].

2.2.1 Sintering Mechanism

Sintering can be classified based on the mechanism that is responsible for the shrinkage or densification. Sintering that is proceeded by solid state diffusion falls under solid state sintering. The driving force for solid state sintering usually comes from the curved surface of the particles and presence of high surface energy. Polycrystalline materials are usually sintered by solid-state sintering while amorphous materials are sintered by viscous flow and are considered to undergo viscous sintering [63]. Another type of sintering that makes use of a transient second phase that exists as a liquid at the sintering temperature is known as liquid phase sintering. The liquid phase under the right conditions can provide a path for rapid transport and, therefore rapid sintering. Finally, processes that make use of an externally applied pressure to enhance densification are classified under pressure assisted sintering.

There are mainly three stages during the entire sintering process; the initial, intermediate and final stage. However, there is no clear distinction between these stages as the process tends to overlap one another but some simplifications can be made to differentiate the individual stages.

In the initial stage, the nanoparticles rearranged into more stable positions by rotating and sliding due to the sintering forces. This will lead to shrinkage and an increase in density. When these particles rearranged, the number of contact points between them increases. This leads to more neck formation among

particles. Neck formation and growth can take place by diffusion, vapor transport, plastic flow, or viscous flow. The initial stage will finish when a neck radius $\sim 0.4\text{--}0.5$ of the particle radius is reached [64].

To analyze sintering, several mathematics models ranging from scaling laws [65], analytical and numerical models have been developed [66]. However, for analyzing the initial stage of sintering, a general equation for the initial neck growth, assuming 2 equal sized spheres can be expressed in a general form of [63, 67]:

$$\left(\frac{X}{a}\right)^m = \left(\frac{H}{a^n}\right)t \quad (2.3)$$

where X is the radius of the neck formed between the particles, m , n are constant that depends on the sintering mechanism involved, a is the initial radius of the particle, H is a coefficient characteristic of the sintering mechanism and t is the time. This general equation for neck growth was first reported by Frenkel [67]. Table 2.3 summarizes the values of m , n and H for different sintering mechanism and Figure 2.6 show the schematic diagram of the different sintering mechanism for a two-particle model.

Table 2.3 Values of m, n and H for Equation 2.3 [68]

S/N	Sintering Mechanism	m	n	H
1	Surface diffusion	7	4	$56D_s\delta_s\gamma_s V/kT$
2	Lattice diffusion from surface	4	3	$20D_l\gamma_s V/kT$
3	Vapor transport	3	2	$3p_0\gamma_s V/(2\pi mkT)1/2kT$
4	Grain boundary diffusion	6	4	$96D_{gb}\delta_{gb}\gamma_s V/kT$
5	Lattice diffusion from grain boundary	5	3	$80\pi D_l\gamma_s V/kT$
6	Plastic flow (by dislocation motion)	2	1	$3\gamma_s/2\eta$

Figure 2.6 Schematic diagram of the different sintering mechanism for a two-particle model

The intermediate stage will then proceed when the pores have attained their equilibrium shapes as determined by the surface and interfacial energies [69]. The reduction in the amount and size of pores is termed as densification. Among these three stages of sintering, the intermediate stage covers a huge portion of the entire sintering process. The final stage involves the removal of the isolated pores until the theoretical density is reached and is accompanied by grain growth where the larger grains tend to increase. The amount of grain growth is

dependent on the sintering parameters and the material itself. Polycrystalline materials generally are sintered by diffusional processes while amorphous materials densify by viscous flow [70]. The driving force for all the sintering mechanisms is the affinity of the material to reduce its chemical potential or energy. This is done through transportation of material from regions of high energy to regions of lower energy. It is known that surfaces, interfaces and grain boundaries of particles have energies that are dependent on the surfaces or its boundary curvatures. Therefore, the overall energy of the material is reduced only when the curvature and number of surfaces are minimized or removed. Such surface diffusion does not produce densification and thus must be avoided. Those that lead to densification are known as volume diffusion of matter from the grain boundaries or from dislocations in the neck region [71].

2.2.2 Challenges of Nanomaterial Sintering

Materials with feature size from 1 to 100 nm are known as nanomaterials [72]. The difference between conventional microscale materials and nanoscale materials is that the latter has significantly larger surface energy. Therefore, reducing the particle size to nanoscale range will lead to a lower sintering temperature.

By definition, sintering is a process that is driven by surface energy minimization. Due to the high surface energy of nanomaterials, the first challenge is the prevention of agglomeration/aggregation of the nanomaterials prior to sintering. Agglomeration is a procedure whereby the nanoparticles are attracted together by weak forces such as Van der Waals or electrostatic forces. Aggregation on the other hand occurs when the nanoparticles are bonded together by solid necks of significant strength such as metallic force. In addition, agglomerations can be re-dispersed by external energy such as mechanical or ultrasonic forces while it cannot be applied to aggregation. Figure 2.7 shows the difference between an agglomeration and aggregation of nanoparticles.

Figure 2.7 Difference between agglomeration and aggregation of nanoparticles during sintering

Another challenge for nanomaterial sintering is the non-densifying diffusion that occurs at the lower temperatures regime. Since these nanoparticles have high surface energy, they will fuse with one another even at room temperature [73, 74]. The temperature at which fusion occurs can affect the degree of densification. This is because if fusion occurs at a lower temperature, the sintering process of the nanoparticles will be controlled by surface diffusion and results in necking between particles. However, there is minimum densification. On the other hand, at higher temperatures, the grain boundary/lattice diffusion that governs the sintering process will lead to densification. Therefore, to attain a high degree of densification, the non-densifying diffusion such as surface diffusion should be avoided. A schematic diagram of densification as a function of temperature is shown in Figure 2.8.

If surface diffusion can occur, the nanoparticles will fuse at a low temperature and will consume the driving force that is needed for densifying diffusion to happen later at the higher temperature region. Such occurrence is very common in nanomaterials due to their high surface to volume ratio that causes surface diffusion to happen at very low temperatures. Hence high heating rate sintering

processes to bypass the low temperature regime is proposed by some researchers [75, 76]. However, the cracking of dies and non-uniform sintering of nanoparticles can occur at high heating rates. This is especially true for passivated metallic NPs since non-uniform removal can lead to non-uniform sintering. The removal of these passivating layers is dependent on a few factors. One factor is the interaction between the passivating ligands and NPs surfaces. If the interaction is strong, the removal may pose some challenges [77, 78]. The second factor can be the NPs size. It was reported by Smith *et. al* [79] that ligands stability on larger NPs is not as good as smaller NPs. Therefore, the removal of passivating layer is easier for the previous. Since the removal of passivating layer is more critical than the size of the NPs, a simple technique to study the effect of the rate of removal of passivating layers and its final microstructures should be carried out.

Figure 2.8 Schematic diagram of rate of densification as a function of temperature

2.3 Nano Cu Sintering and its Thermal Stability

2.3.1 Sintering Temperature

Die attach materials used in power electronics devices are required to possess good mechanical, electrical and thermal properties. In addition, it must have good reliability against thermal cycling and fatigue. Metallic nanoparticles have been deemed as a possible alternative for high temperature Pb-based solder [57]. These metallic nanoparticles can be processed at a lower temperature due to their high surface energy yet they have similar properties to those of the bulk metals or alloy after sintering [47]. Due to the high surface energy of the nanoparticles, to prevent unwanted sintering at room temperature, these metallic nanoparticles are usually capped with an organic layer to prevent fusion. Therefore, though previous studies on the bondability of Cu NPs were carried out, they were either run at much higher temperatures, i.e. 230°C and above or under vacuum or forming gas environment [30, 46, 80, 81]. Such high temperatures and special environment are needed because the capping layers used on the nanoparticles can only be removed completely at higher temperatures. Failure to remove these organic layers would hinder subsequent fusion of the nanoparticles [61]. Though room temperature sintering of Ag NPs with diameter around 8 nm has been demonstrated, it has a low shear strength of ~ 8 MPa [82]. In another Ag NPs study, the fusing of Ag NPs was observed at 150°C for a particle size of 20 nm but to achieve a good shear strength, a temperature of >230°C is needed [83, 84]. Such processing techniques will incur a higher operational cost and is not suitable for polymeric substrates. Processing of Cu NPs at 200°C or below and its ability to integrate into the current solder based process equipment and parameters have not been widely studied yet.

2.3.2 Heating Rate

Another factor that affects the sintering of NPs is the heating rate of the NPs paste up to the peak sintering temperature. As mention in Section 2.2.2, NPs are prone to fuse when the capping layers are removed. Hence if fusion can occur at lower temperature, surface diffusion is likely to occur. However, this does not contribute to the densification of the sintered joint. Thus, a faster heating up rate

will promote a denser structure since surface diffusion is the dominant mechanism at low temperature while grain boundary or lattice diffusion dominates at the higher temperatures regime. This means that at higher heating up rate, it minimizes aggregation of nanoparticles during the heating up phase as it bypasses the low temperature regime faster to reach the peak sintering temperature. Therefore, these nanoparticles will not aggregate or agglomerate into a larger effective radius during heating up and will be able to keep its nano-sized properties till the peak sintering temperature to achieve a denser structure subsequently. On the other hand, the heating rate must not be too fast as it must provide sufficient time for the outgassing of solvent. A rate of $\sim 10 - 20^{\circ}\text{C}/\text{min}$ appears to be the optimum heating rate for Wang *et al.* [9] although others have used higher heating rates of $60^{\circ}\text{C}/\text{min}$ with an added pressure on the die so that the dies are not lifted during sintering [85]. In addition, a higher heating up rate might not result in uniform removal or decomposition of capping layers as the thickness of the sintered joint is usually not considered. When heating rates are high, those NPs that are located near to the surfaces will fuse first due to faster removal of capping layers as compared to NPs located at the bottom of the layer. When the top layer of the NPs has fused, it might minimize the number of paths available for subsequent removal of organic materials. This can potentially lead to a non-homogenous sintered layer/joint. Therefore, besides a high heating rate, an effective method of removal of the capping layers faster and uniformly must be investigated.

2.3.3 Sintering Time

As mentioned previously, sintering is a diffusion-controlled process. Hence the duration of sintering will influence the sintered NPs joint. However, the optimum time for every type of NPs and joint design varies. For Wang *et al.* [9], shear strength of $17 - 18 \text{ MPa}$ was reported after 1 hour of sintering of the Ag NPs. However, for Knoerr *et al.* [35], shear strength of 40 MPa was achieved when sintering time increased from 5 to 60 secs and the density of sintered joint increased from 68% to 75%. The occurrence of such fast sintering is due to the fusion of Ag NPs once the capping layers were decomposed or volatilized under heat and/or pressure. Therefore, the rate of capping layer removal has a huge influence on the sintering mechanism of NPs. This rate of capping layer removal

is affected by the type of capping layer used and its affinity with the metallic NPs surfaces. It is quite difficult to compare the mechanical properties of these sintered joints and the NPs as they are synthesized and capped differently. Such differences could contribute to difference in sintering parameters such as temperature and/or time to obtain a strong sintered joint. Therefore, a quick and easy method should be used to characterize all the different types of capped metallic nanoparticles to enable one to tune the processing parameters appropriately.

2.3.4 Stability of Cu Joint

In addition, most studies focus only on the feasibility of using these Cu NPs for low temperature processing application, high power electronics and/or replacing Sn-Pb solder [30, 57]. To adopt the usage of Cu NPs paste to replace high temperature solder materials, the long-term stability of sintered Cu joints must be studied in detail. This can be done by measuring the die shear strength after annealing at elevated temperature for a specific duration. Though it is reported that increase in sintering time enhances Cu densification, pro-long annealing could lead to degradation taking place that can affect the overall shear strength. In some of the thermal reliability studies on sintered Cu NPs joints between Cu or Au surfaces, it has been shown that these sintered Cu NPs joints are able to withstand a higher temperature than conventional solder or have a better shear strength after prolong annealing due to no formation of inter-metallic compounds (IMCs) within the joints itself [86, 87]. However, the relationship between grain growth of these particles, changes in the grain orientation, and porosities evolution with shear strength are still not studied.

2.4 Sintering Behavior of Cu NPs and Removal of Organic Materials

As mentioned in Section 2.3, various researcher groups synthesized their Cu NPs uniquely with different passivating layers and dispersed in different additives, hence the optimum sintering profile used will vary. In general, the sintering of these capped metallic nanoparticles goes through two major steps. The first step involves the decomposition or volatilization of solvents and capping molecules on the surfaces of the NPs. After which, fusion of NPs which is observed as the

formation of necks between NPs will occur [57, 61, 75]. Most groups have used TGA and DSC/DTA to understand the sintering behavior of their NPs used [46, 59, 88]. Such equipment can quantify the loss of organic materials and onset of fusing during constant heating up and/or isothermal annealing under inert or air condition. However, such technique does have its shortcomings. Firstly, the heating mechanisms in this thermal analysis equipment and the actual oven or hotplate used during sintering are different. In addition, for bonding application, a sandwiched structure is used. Hence, the removal path of the volatiles will be different from an open structure. The removal of solvent and capping layers under a sandwiched structure is even more challenging when the die size increases [75]. All these differences might lead to some discrepancy in the temperature of volatilization and/or decomposition of solvent, capping organic materials and subsequent fusion of the NPs. Secondly, using TGA or DSC/DTA will require an additional step and time prior to sintering. Moreover, the heating rate that is set when using such thermal analysis equipment is usually about 10°C/min. However, based on literature, many researchers had tried higher heating rates sintering of NPs to benefit from its high surface energy i.e. >20°C/min [85]. Such high heating rates are usually not compatible with the TGA or DSC/DTA used. Therefore, for such situation, it is hard to use the conventional instrument to design a suitable sintering profile to study the sintering behavior of NPs. Therefore, other simple and direct quantifying techniques should be considered to understand the sintering behavior of these NPs paste when they are subjected to different heating profiles, environment and sintering structures.

2.4.1 Removal of solvent and capping layers

Prior to fusion, effective removal of solvent and other organic materials within or on the NPs should be completed. These solvents are added into the NPs paste formulation to achieve a suitable viscosity for dispensing the material for die-attach applications. The weight percentage of metallic NPs is usually more than 50% with percentage as high as 80% [57, 87]. Usually, mixtures of solvents and/or surfactants are used within the NP paste formulation to provide viscosity adjustment, steric resistance between NPs to prevent agglomeration prior to

sintering. Hence, these organic contents might not be removed easily and non-homogenous sintered layer can be observed [61]. This means that the densification rate across sintered joints is different. Though a longer annealing time, higher temperature or even application of pressure can help to improve the situation, it might not be feasible in actual applications. Some researchers have proposed a 2-step sintering method to ensure uniform microstructures. The first step of the sintering is done at a lower temperature to remove the solvent present. Next, a high heating up rate is used to ramp to the peak sintering temperature for the next step of sintering [57]. Other method of improving the removal of capping layers is to introduce a 2-step sintering under different environment. As reported by Yi *et al.* [89], since the removal of capping molecules is minimum under vacuum condition, the heating up of NPs is done under vacuum. Once the peak sintering temperature is reached, air would be introduced. This will ensure that both removal of capping layer and the fusing of NPs happen at the peak sintering temperature. Another method reported by Jang *et al.* [61] on their amine-capped Au NPs is the introduction of N₂ gas that is bubbled through formic acid. They did a comparison on the effect of different types of sintering environment (air, N₂ and N₂ with formic acid) on the microstructure of the sintered Au NPs. It is observed that those that are sintered with formic acid have more coalescence and grain growth than those that were sintered under air or N₂ at the lower sintering temperature of 200°C. For Au NPs that were sintered under air or N₂, grain growth was only observed when sintering was done at 290°C. The ability of sintering at lower temperature when formic acid is introduced is due to the etching of amine molecules by the formic acid. This helps to remove the capping layer faster and thus able to sinter at lower temperature. However, low level of densification is observed due to large number of pores being distributed within the sintered Au film. Though this technique helps to remove the capping layer faster, large pores were observed and this leads to a higher resistivity as reported.

Therefore, based on all these literature, a more detailed study on the removal of organic materials with temperature, time and heating rate should be carried out. The resultant microstructures at different stages of sintering should also be given some attention as it would relate to the final mechanical strength of the sintered

joint. Since the removal of organic materials has a huge influence on the final microstructure of the sintered joint, detail study should be carried out to study this initial step of the sintering process. This is very crucial when the sintering of NPs is done at a higher heating up rate to achieve a more homogenous sintered layer.

2.5 PhD in Context of literature

Based on the questions raised in the previous section, this work aims to develop and study on low temperature bonding process ($\sim 200^{\circ}\text{C}$) using Cu NPs for robust interconnection and die attach applications. A deeper understanding on the effects of bonding parameters such as ramping rate, bonding pressure and soak duration at peak temperature of 200°C on the joint strength will be studied. The bondability of joints obtained from Cu NPs sintering will be studied mainly by characterizing their respective shear strength, electrical resistance during annealing and co-relating it with its resultant microstructures and porosities. The onset temperature of volatilization and fusion of these Cu NPs that result in different microstructures will be an area of interest. These changes in the final microstructure and its effect on mechanical and electrical properties can shed some light to future metallic NPs paste development that will be used in interconnections and die-attached applications. Joint stability test such as isothermal ageing test 150°C up till 1000 hours in air is used to study and understand the mechanical properties and microstructure evolution of the sintered Cu joint for its potential to be used to replace current solder material. A deeper understanding in terms of grain growth and orientation evolution and degree of oxidation over time will also be looked into as they can affect the long-term reliability of the sintered Cu NPs. The final aim of this work is to apply this novel Cu NPs paste as a die-attach material for actual high power LEDs modules. Its initial performance will be directly compared with commercially available AuSn solder. Reliability tests such as long-term high temperature storage and thermo-mechanical test would be carried out to investigate the reliability of the Cu NPs joints. Some of its challenges faced will also be discussed.

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Chapter 3

Experimental Methodology

This chapter describes the experimental and characterization techniques used in this project. The rational, limitations and assumptions made with each technique would also be discussed. This includes the technique of post-processing the as-synthesized copper nanoparticles, the reasons for different types of surfactant added and sample preparations for subsequent experiments and characterizations. Thermal characterizations of these Cu NPs were carried out using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). These techniques are used to understand the basic thermal behavior of the Cu NPs when subjected to different heating profiles. A DIY furnace for sintering of Cu NPs paste that is coupled with in-situ electrical resistance measurement is used to study the change in electrical resistance under various suitable sintering conditions that were previously derived from the thermal characterizations results. The microstructures of the sintered Cu NPs from different sintering conditions were analyzed using a field emission scanning electron microscope (FESEM) coupled with focus ion beam milling (FIB) capability. This allows the top surface morphology and cross-sectioned of the sintered Cu NPs layer to be studied concurrently. Lastly, the working principle of an X-ray diffraction (XRD) method was outlined and justified for its usage to understand grain growth and crystallite orientation of sintered Cu NPs.

3.1 Rationale for Selection of Methods

The main objective of this work is to develop an understanding of the basic properties and behaviour of the organic passivated metallic NPs and demonstrate its feasibility to be used for low temperature process applications. Therefore, initial post-processing of these as-synthesized Cu NPs and understanding the thermal behaviour of the Cu NPs is necessary. Since these Cu NPs is targeted towards the die-attach and/or 3D interconnect applications, suitable viscosities of these Cu NPs paste for different applications have to be adjusted by adding suitable type of solvents and surfactants. In addition, to form a conductive metallic network at low processing temperature ($\leq 200^{\circ}\text{C}$), these organic materials present within and on the Cu NPs have to be completely removed at or below 200°C . Hence, the first step is to establish a detailed understanding of the thermal behavior of the Cu NPs paste after adding suitable solvents and surfactants when it is subjected to different sintering conditions. To do this, TGA and DSC are often used to study the basic thermal characteristics of the organic materials as it is a fast and simple technique to study the thermal decomposition and critical thermal activities such as melting, enthalpy of reaction and thermal degradation respectively with respect to time or temperature. In addition, the environment of test can be controlled to be inert or at atmospheric environment.

A suitable thermal profile is selected after the basic thermal characteristics of Cu NPs are known. Since the main purpose of this study is to develop a lead-free die-attach material for high power applications and/or 3D interconnects, the mechanical, electrical properties and the microstructures of the material after processing are important. The transition from high electrical resistance to a conductive metallic network depends on the removal of organic materials and the fusion of these Cu NPs. Hence an *in-situ* resistance measurement is set-up within the sintering oven to enable the study of resistance change with temperature, time and environment. Such study provides a fast and effective way to study the electrical property directly during the sintering process. Microstructure evolution of the Cu NPs can also be directly studied by freezing the respective microstructure when a critical temperature during sintering is reached. FESEM coupled with a FIB that comes with milling capability is used to study the top and cross-sectioned microstructures.

To enable the use of such sintered Cu NPs for die-attach and interconnect applications, the long-term thermal stability of the joint needs to be understood. Grain size and texture of the aged Cu NPs joints which have a direct influence on mechanical and electrical properties, needs to be understood and characterized. Therefore, μ XRD is carried out to understand the grain growth and crystal orientation with time. This technique is chosen due to its capability to analyze small grain size and small localized area of interest.

3.2 Post-Processing and Sample Preparation of Cu NPs

3.2.1 Washing of as-synthesized Cu NPs

The Cu NPs paste, Cuquantumfuse™, was synthesized by Dr Alfred A. Zinn *et al.* at Lockheed Martin ATC Corporation [1]. They were kept in a 50 ml syringe for ease of transportation, storage and dispensing. Prior to sintering, washing of the raw Cu NPs is necessary to remove unwanted and unreacted substances left behind after the synthesis process. After the washing procedure was completed, additives which include low boiling points solvent and some surfactants were added to adjust the viscosity of the Cu NPs paste. It was then transferred into a 10 ml syringe and mixed between 2 syringes before using it for subsequent studies. A schematic diagram on the washing procedure is shown in Figure 3.1.

Figure 3.1 Schematic diagram of the post-processing of Cu nanoparticles before sintering

**All surfactants used are proprietary information and will not be disclosed in this thesis.

3.2.2 Sample Preparation for Electrical Resistance Studies

A simple electrical test structure is constructed using a glass slide, copper and Kapton tape. It was connected to a Kiethley 2400 sourcemeter. A 4-point probe connection was set-up for the electrical resistance measurements as shown in Figure 3.2. A sourcing current of 1 mA was applied and the resistance was measured during the sintering process. The main objective for carrying out this electrical resistance measurements is to provide a fast and effective way to understand the sintering behaviour and observe any abnormal behaviour of the Cu NPs when subjected to different sintering conditions through monitoring the resistance *in-situ*. A picture of the test structure for bonding and non-bonding testing is shown in Figure 3.2.

Figure 3.2 Pictures of the simple electrical test structures and set-up

However, there are some advantages and limitations to the use of such test structures. The advantages as mentioned earlier are the ease of creating such test structure and the variable area of the dispensed NPs can be adjusted with the copper and Kapton tape for various die size characterisations. However, the thickness of the Cu NPs is rather thick ($\sim 80 \mu\text{m}$) as it is dependent on the

thickness of the tapes used. The thickness of bonded layer that is applicable is usually $<10\text{ }\mu\text{m}$. Since the layer spread onto the test structure is thick, it will be prone to cracking during the intermediate stage of sintering where shrinkage and densification take place. When cracking occurs, there is a discontinuity within the sintered Cu. This prevents the resistance of the Cu NPs to be measured properly. Hence this method is good for studying the initial sintering process of the Cu NPs whereby minimum shrinkage and densification is observed.

In addition, the thickness and thermal conductivity of glass and Si chip have to be considered as well in setting the temperature. When testing with different substrates, the heating profile and set temperatures have to be adjusted accordingly. Prior to measuring the electrical resistance, a thermocouple was placed onto the test structure to ensure that the actual temperature on the substrate and the set temperature of the temperature controller is similar to achieve a comparable and unbiased result.

3.2.3 Sample Preparation for Bonding Applications

The feasibility of using these Cu NPs as a die-attach material is first proven on a similar metallic material surface, Cu. Hence, SiO_2 wafers were sputtered with a 10 nm-thick TiO_2 for adhesion purpose between Cu and SiO_2 . A 500 nm thick Cu was sputtered onto the TiO_2 layer. After which the wafer was diced into 1 mm X 1 mm and 5 mm X 5 mm chip and substrate, respectively for subsequent bonding purposes. A 1 mm X 1 mm area chip was selected due to several reasons. One of the reasons is the ease of controlling the wetting of Cu NPs paste across the entire bonding area. Secondly is to avoid or minimise non-uniform volatilisation across bigger die area as it is harder for solvent located at the inner area of the die to volatilise during the sintering process [2]. Hence to minimise the effects due to die size dimension, a 1 mm X 1 mm die was chosen.

Prior to bonding, the chips and substrate were washed with acetic acid to remove copper oxide from the surface [3]. Otherwise, the bonding between substrate and Cu NPs would not be good as the oxide could hinder fusion between bonding surfaces and Cu NPs. No further test was carried out that to verify the

“cleanliness” of the Cu surface after washing and it is assumed to be oxide-free and consistent for all bonding samples.

After preparing the bonding dies and substrates, small amount of Cu NPs paste (~10 mg) was dispensed manually onto the 5 mm X 5 mm substrate and a Mayer rod was used to spread the Cu NPs paste evenly across the entire substrate. The 1 mm X 1 mm die was then placed on top of the substrate with some light pressure exerted to ensure good contact and spread across and between the bonding surfaces. Therefore, it is observed that the viscosity of the Cu NPs paste plays an important role for the initial spreading across the entire bonding area. A good contact between bonding surfaces is essential for forming strong bonds especially at the bonding interfaces. The thickness of the paste was kept between 5 – 10 μm as thicker joints would induce more cracks due to shrinkage during sintering.

3.3 Characterization of Cu NPs

3.3.1 Thermal gravimetric analysis (TGA)

Thermal gravimetric analyses (TGA) of the Cu NPs were carried out on TA Instrument Q500 to characterize the thermal characteristics of the Cu NPs at different temperatures and time. TGA is commonly used for various thermal analyses such as (1) characterization of decomposition patterns, (2) studies on degradation mechanisms and reaction kinetics, (3) loss of organic content in samples as a function of time or temperature, and (4) mass loss or gain due to oxidation, evaporation or decomposition. TGA can be carried out under inert ambient such as nitrogen or argon or in air condition. The weight of the samples is recorded as a function of changing temperature or time. A schematic diagram of a TGA is shown in Figure 3.3. In this project, it is mainly used to determine the loss of organic content due to volatilization as a function of temperature or at different heating rates by observing the change in weight. All tests were run under nitrogen (N_2) condition to prevent oxidation of copper during the process. The flow rate of N_2 used was 60 SCCM. The system was cooled naturally after the experiment. The temperature range tested was between 25°C – 300°C. 10 mg of the copper nanoparticles paste were placed on a tared aluminum pan. The results were used to determine the minimum temperature used for sintering of

the Cu NPs paste in subsequent experiments. The onset temperature of volatilization and sintering for each heating rate was an average of three runs.

However, there are a few limitations and assumptions made when using this technique. One of the limitations is the inability to effectively heat up at a higher heating rate i.e. $>10^{\circ}\text{C}/\text{min}$. Though the program allows a heating rate up till $40^{\circ}\text{C}/\text{min}$, the actual temperature and the set temperature do not match once a higher heating rate is adopted. This is due to the limitation of heating element capability in the TGA equipment. The second limitation is that the un-passivated Cu NPs are susceptible to oxidation. Though the test was carried out at inert condition, oxidation could occur at the higher temperature, $>200^{\circ}\text{C}$, due to poor control of the furnace ambient. An increase in weight was usually observed. Therefore, thermal characteristics of these Cu NPs at higher temperature range or even prolong isothermal annealing test are hard to achieve.

Based on the layout of the TGA equipment, the heating mechanism is largely dependent on convection process since the sample is not placed directly on the heating element. In our study, both conduction and convection play a role in the sintering process. Hence the difference in heating mechanism should be kept in mind when comparing results.

Figure 3.3 Schematic diagram of a TGA

3.3.2 Differential Scanning Calorimetry (DSC)

From the TGA results, weight loss as a function of temperature and time is known. However, some thermal transition activities such as melting and fusion do not lead to a weight change, but is accompanied by heat flow. This will enable the user to identify precisely the phase transitions of the samples and other chemical reactions that do not lead to weight change. To identify the onset fusing temperature of the Cu NPs, DSC measurements were carried out on a DSC TA Q10 under N₂ atmosphere. Samples were run from 25°C to 300°C. 10 mg of the Cu NPs paste were placed in a pre-weighed aluminum hermetic sealing pan. DSC uses a feedback loop to maintain the sample at a set temperature while at the same time measures the power needed to do this against the reference sample. Hence the result of heat flow against time or temperature can be plotted. In addition, DSC data can be used for determination of the enthalpy and specific heat capacity (*cp*) of the tested material. In this study, the DSC measurements were used to correlate with the TGA data. With the combination of both, it provides an overview of the thermodynamics transitions that happen during the heating up process of the Cu NPs within the set temperature range. Figure 3.4 shows the schematics of a DSC setup.

Figure 3.4 Schematic diagram of a DSC

However, since TGA and DSC were run separately, there might be some discrepancy arising from different amount of samples since it would have some effect on volatilizations and fusion of Cu NPs. Hence to minimize the errors,

similar amount of Cu NPs and the same batch of samples were used for both types of characterizations.

3.3.3 *In-situ* electrical resistance measurements

Though the general thermal characteristics of the Cu NPs are known, it is limited to heating rate below 10°C/min due to equipment constraint. The thermal characteristics of these Cu NPs at higher heating rates were not achievable based on previous techniques. In addition, the characterizations were done separately from the actual sintering equipment. Hence some differences in terms of heating mechanism might cause inaccurate observations. Thus, the ability to carry out an *in-situ* thermal characterization during the sintering process will be the most accurate to indicate the actual mechanism.

As explained earlier, the sintering of the Cu NPs is based on the transition from an insulator that is made up of many organic passivated metallic NPs to a conductive metallic network after thermal treatment. Such transition would cause the electrical properties of the Cu NPs to change. Hence *in-situ* electrical resistance measurements were carried out in a heating furnace equip with fast heating up rate to as a proxy to monitor the transitions of the Cu NPs. With such measurements, the electrical resistance of the Cu NPs will be measured during heating up and isothermal annealing. Such information can be used to correlate with the Cu NPs fusion process at different process conditions. Details on the sample preparation and the type of electrical test structure used was mentioned Section 3.2.2.

Before thermal treatment, high electrical resistance is expected due to the presence of organic materials as observed from the TGA data (~20 wt. %). During heating, the removal of organic materials present within and on the Cu NPs would cause the Cu NPs to fuse due to their high surface energy. Therefore, different onset temperatures of volatilization and fusion at various sintering conditions can be gathered accordingly due to a sudden change in electrical resistance of the Cu NPs during sintering.

With this characterization technique, it is assumed that the thickness of the Cu NPs layer remains largely constant and similar for all samples. Since resistance

instead of resistivity is measured, the thickness of the Cu NPs is assumed to be constant for all samples and does not have a huge influence on the onset temperatures of volatilization and fusion. Based on the data derived from this technique, a model is developed to predict the dominant sintering mechanism when subjected to different heating up rates. In this model, minimum or no shrinkage of equal sized spherical Cu NPs is assumed.

3.3.4 Shear Test

After bonding the Si-based chips with Cu NPs, shear testing was done to measure the shear strength of the bonded joint. Figure 3.5 shows the setup of shear tester. The mechanical shear strength of the bonded joint is characterized by the die shear test. All shear testings were carried out using a shear tester (DAGE 400) with a maximum load of 5 kg.

Figure 3.5: Shear test setup

Die shear testing is the process of determining the strength of adhesion of a die to a substrate, with a stress being applied to a die in parallel to the plane of the die attach substrate. This can result in a shearing stress at 3 possible locations:

1. between the die-die attach material interface,
2. within the die-attach material itself, and
3. between the die attach material-substrate interface

The failure location of each sample must be noted and analysed separately as it could indicate how the changes in bonding parameters affect the failure location. During shear testing, the force applied to the die must be sufficient to shear the die from the substrate or twice the lower specification limit for the die shear strength. The direction of the applied force must be perpendicular to the die edge and parallel to the die attach or substrate plane. After the initial contact has been made and the application of force starts, the relative position of the tool should not change throughout the shearing process. The tip of the probe should not contact both the die attach material and the substrate. All these are represented schematically in Figure 3.6. To achieve statistically reliable results, 6 measurements were taken for each data point.

Figure 3.6 Schematics diagram of the shear test setup

3.3.5 Field Emission Scanning Microscopy with Focused Ion Beam Milling Capability

After understanding the thermal characteristics of the Cu NPs at different sintering conditions, microstructure analysis is needed to explain the difference in thermal and electrical properties of the Cu NPs before and after sintering. Microstructures analysis is usually done using a Scanning Electron Microscope (SEM) or Field Emission Scanning Electron Microscope (FESEM). Both are electron microscopes that are capable of imaging the sample surfaces by raster scanning over the surfaces with high energy beam of electrons. These electrons

will interact with the atoms of the samples and produce signals that contain information such as compositions and topography. The difference between a SEM and FESEM is the type of emitter. SEM uses a thermionic emitter while FESEM uses a field emitter. The difference between them is that electrical current is used to heat up the filament in the thermionic emitters. The electrons will escape from the filament material when the heat is sufficient to overcome the work function of the filament material [4]. In addition, such thermionic sources usually have a relative low brightness and suffer from thermal drift during operation. However, all these limitations can be solved by using a field emission emitter to generate electrons. A Field Emission Gun (FEG) does not heat the filament. The principle of electron emission in a FESEM is based on having a huge electrical potential gradient in the filament material [5]. The FEG is usually a wire of Tungsten (W) made into a sharp point that has a small tip radius (~ 100 nm), so that the electric field can be concentrated to an extreme level. As a result, the work function of the material is overcome and allows the electrons to leave the cathode. Therefore, by using such emitter in a FESEM, it is able to produce a cleaner image, less electrostatic distortions and spatial resolution of < 2 nm, which is much better than a SEM [5]. With such a high spatial resolution, it is commonly used for characterization of nanomaterials structures.

The FESEM coupled with a FIB system used in this project is FEI Nanolab DualbeamTM 600i. This equipment is able to perform high resolution field emission scanning electron microscopy, focused ion beam cutting and energy dispersive x-ray spectroscopy (EDS). The full specification can be found here [6]. In this project, this system was mainly used to carry out top and cross-sectioned analysis of the sintered Cu layers. A protective layer of Pt was deposited on the sample at the place of interest prior to milling. A $10\text{ }\mu\text{m}$ length and $1\text{ }\mu\text{m}$ width and height were typically being deposited. After which a “multi-pass” cutting was performed to make a coarse milling at the area of interest. The Ga ion current and voltage used for this cutting was set at 9.3 nA and a 30 kV , respectively. After the cut, cleaning of the exposed area will be carried out for better imaging. The mode used for cleaning was “clean cross section” with a current of 93 pA and voltage of 30 kV . Figure 3.7 shows a typical cross sectioned

image of a sintered copper layer on a Si substrate after cleaning. However, due to the reactive nature of these sintered Cu NPs, care should be taken when doing ion beam milling as unintentional fusing of these Cu NPs by the Ga ion-beam irradiation can take place. This eventually could affect the final microstructure when comparing against different samples.

Figure 3.7 Cross-sectioned SEM image of a sintered Cu NPs layer

3.3.6 X-ray diffraction (XRD)

Apart from microstructure, the crystalline structure and the grain growth evolution of the sintered or aged Cu NPs is an important piece of information for further study in the mechanical, electrical and thermal properties. X-ray diffraction (XRD) is a non-destructive technique for characterizing crystalline materials in terms of its phase identifications and preferred crystal orientations (texture). In addition, it can also provide structural information such as the crystallinity, strain, crystal defects and average grain size of the materials [7].

The basic principle of a XRD is based on Bragg's law. When an incident beam of X-ray comes into contact with the crystalline sample, they are diffracted by the atomic planes. The X-ray diffraction peaks that are produced are due to the constructive interference of a monochromatic beam of X-rays scattered at specific angles from each of the lattice plane. The constructive inference can be deduced by Bragg's equation as given by

$$n\lambda = 2d\sin\theta \quad (3.1)$$

where d is the spacing between parallel lattice planes, θ is the angle between the incident X-ray and lattice planes, λ is the wavelength of the incoming X-ray and n is an integer. Figure 3.8 shows the pictorial representation of Bragg's law.

Figure 3.8 Schematic diagram of Bragg's law [8]

The peak intensities are then determined by the distribution of atoms within the lattice. Therefore, these x-ray diffraction patterns are unique periodic atomic arrangements within a particular material and can be cross-referenced with the database provided by any XRD software to determine the structural information of the desired sample. In addition, the width of the peak produced in XRD has also been used to estimate grain size. This equation is commonly known as the Scherrer equation [9]. It can be written as

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta} \quad (3.2)$$

where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; K is a dimensionless shape factor, which has a value close to unity but varies with the actual shape of the crystallite; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM) in radian, after subtracting the instrumental line broadening; θ is the Bragg angle.

With this equation, a good estimation of the crystallite size can only be done when there is no lattice imperfection in the crystal since it can cause peak broadening as well [10]. In addition, there are some limitations of XRD characterisation. Firstly, depth profiling is not possible. Hence, structure comparison across sintered layer depth is not possible. Therefore, in this study, it is assumed that the crystal structure is similar across the sintered layer. Since depth profiling is not possible, specific area of scan is important for observing structure difference across similar samples. However, due to its large spot size area scan, it is challenging for characterising the bonded structures in this study.

To overcome this problem, micro-XRD (μ XRD) coupled with Synchrotron radiation was used as it is able to scan a smaller area. The grain growth and texture of the fused Cu NPs after ageing for 1000 hours at 150°C were studied using synchrotron radiation micro-beam X-ray diffraction at Advanced Light Source, Berkeley. The beamline used is 12.3.2 with a wavelength of 1.033 nm. These samples were scanned under a 1 μ m size polychromatic beam with an energy band pass of 5 – 24 keV. The wavelength of the radiation used is 1.0332 Å and the diffraction patterns were processed using XMAS software [11]. All the XRD line profiles were Lorentzian in shape which is typically used for nano-crystalline material [12].

3.4 Overview of Methodologies

All experimental methodology used in this thesis have been described and explained in this chapter. The rationale and limitations of each processing and characterisation method must be considered for better data collection, analysis

and model building in the subsequent studies. The availability of resources must be taken into considerations at times. Due to limited time and resources, the *in-situ* electrical resistance of the Cu NPs on the DIY test structure is the approach taken to understand the sintering mechanism. With each characterisation tool comes with its own set of limitations, it is sometimes beneficial to adopt a few characterization tools for drawing a more accurate conclusion as they complement the shortcomings of the other techniques. This is why with the combination of TGA, DSC, *in-situ* electrical resistance measurements and microstructure analysis, it might be able to provide a better explanation of the sintering behaviour of these Cu NPs. This is very important when dealing with a novel material where little is known. In the following chapters, the results and discussion of each experiment would be explained in detail.

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Chapter 4

Sintering and Densification Behavior of Nano-sized Copper Particles

This chapter discusses about the sintering and densification behavior of nano-sized copper particles. TGA, DSC and in-situ electrical resistance measurements during sintering are used to study the thermal, physical and electrical changes that arise from different processing parameters. It is observed that the heating rate has a direct influence on the onset temperature of volatilization of organic materials (T_E), which then affects the subsequent fusing temperature (T_F) of the Cu NPs and the resultant microstructure. Moreover, the rate of volatilization of organic materials under different environment such as inert, vacuum and formic acid vapor has a direct impact on the rate of removal of the passivating layers on the Cu NPs, as well as on the uniformity of removal. The different process parameters and environment thus affect T_E and T_F , the electrical resistance of the sintered Cu, and its microstructure such as size and amount of porosities of the sintered Cu layer. Hence, this chapter will provide in-depth studies on the relationship between the process parameters and the final microstructures of sintered Cu NPs.

4.1 Introduction

Metallic nanoparticles (NPs) have been a field of interest owing to their unique characteristics that are different from their bulk state, such as high surface energy. Although noble metallic nanoparticles such as Au and Ag are commercially available, Cu NPs may be a cheaper alternative with superior properties. However, Cu is known to be very sensitive to oxidation. Hence, different types of passivating materials for Cu NPs and ways to eliminate Cu oxidation have been widely studied [1-6]. Some research groups have been actively developing metallic nanoparticles paste, Ag or Cu, as a bonding material for electronics devices [7-9]. Besides being a potential substitute for solder materials due to its low processing temperature, it too has gained some attention in the flexible electronics sector. Hence, printable inks which comprise of these metallic nanoparticles have also been developed in recent years [10, 11].

It is reported that the melting point of NPs for most elements reduces almost linearly with the inverse of its radius [12]. However, in Chapter 2, it is mentioned that if the diameter of the particles is not sufficiently small, its melting temperature will be similar to its bulk melting temperature. Hence in this study, the size of the nanoparticles that were used consists of Cu NPs with different sizes as shown in Figure 4.1(a). Therefore, one can expect sintering to occur in solid state and surface energy minimizing is the main driving force of these metallic nanoparticles to fuse and form a conductive path at a lower processing temperature since majority of the NPs are >50 nm. Meanwhile, organic passivating materials are required to prevent unwanted fusion among the particles or oxidation prior to sintering. Although low temperature sintering behavior of silver (Ag) NPs has been studied extensively [13-16], few have reported on Cu NPs [5, 17]. It is known that Cu oxidizes easily in air which lowers its electrical conductivity. Therefore, these Cu NPs, which are passivated with organic materials to prevent oxidation and fusion, is an insulator prior to sintering. To achieve the desired electrical and mechanical properties of the sintered NPs, these passivating layers must be completely removed during the thermal treatment to allow fusion among these NPs [18, 19].

Presently, most literatures have indicated that a processing temperature of more than 230°C is required for good Cu NPs sintering under inert conditions [3, 10, 11, 20-22]. High temperature is usually needed for the decomposition, desorption or volatilization of the organic additives present within the Cu NPs. Some groups have proposed to reduce the size or change the shape of the nanoparticles to take advantage of thermodynamic effects to lower the processing temperature [23, 24]. However, depending on the final applications, the reduction in particle size might not be feasible for thin film application. In thin film application, it is better to use larger nanoparticles as a denser film can be achieved [25]. However, bigger nanoparticles will need higher sintering temperature and/or longer time to be fused, while in manufacturing conditions, the sintering requirements are shorter processing time and lower temperature. As a result, smaller particles size can help to optimize the process condition but may not lead to a dense film after sintering. Therefore in this study, a mixture of Cu NPs sizes as shown in Figure 4.1 were used so that it could be fused at a lower temperature and shorter time, yet at the same time achieve a dense structure.

The solvent used in the formulation of the Cu nanoparticles paste is an alcohol that can evaporate at low temperature. The surfactants were chosen based on its volatilization temperature as the aim is for them to be removed during sintering at 200°C. Another consideration factor is that these surfactants must be able to cover the surface of the nanoparticles during synthesis to prevent agglomeration (weak electrostatic force). A simple schematic diagram of the ligands on the Cu NPs is added as Figure 4.1(c) in the thesis as below. Details of the formulation are proprietary information and thus could not be disclosed in the thesis.

Figure 4.1 (a) TEM image of Cu NPs used (b) Zoomed-in image of a Cu NP (c) Schematic diagram of how the ligands are attached on Cu NPs

Though there are challenges in integrating these Cu NPs into current reflow processes, its ability to be sintered at a relatively low temperature with substantially good electrical, thermal and mechanical properties is a major advantage [26]. Hence, detailed studies on the effects of sintering parameters such as sintering temperature, time and type of ambient have been carried out [27-29]. The relationship between heating rate and densification of nanoparticles has been reported [28, 30, 31] and it is stated that higher heating rate is preferred to achieve a denser microstructure as it bypasses the low temperature regime [16]. However, these studies were mostly done on non-metallic NPs that are not passivated with organic materials. For metallic NPs that are passivated with

organic materials, the sintering of particles requires an additional step of removing the passivating layers prior to fusing. Therefore, whether a higher heating rate is preferable for these passivated metallic particles as well will be an interesting area to explore.

Hence in this chapter, the microstructure evolution of these Cu NPs sintered to a maximum temperature of 200°C at different heating rates, and isothermal annealed at 200°C for 5 – 30 minutes for subsequent fusion and densification under N₂ condition will be studied. In addition, sintering of these Cu NPs under acid-based environment were carried out to study the thermal stability of the passivating layers under various type of ambient.

4.2 Principle Outcomes

4.2.1 Characterizations of Cu NPs

Figure 4.2 shows the TGA results overlaid with the *in-situ* electrical resistance measurements at a heating rate of 10°C/min under N₂ ambient. A large percentage drop in weight (~16 wt%) was observed from 25°C – 100°C while a smaller percentage drop (< 5 wt%) continued from 100 – 230°C. A total weight loss of 18% was recorded.

Figure 4.2 TGA and electrical resistance curves of Cu NPs heated from 25°C to 300°C

This overall weight loss of 18% is possibly due to the removal of organic materials within the Cu NPs paste. Between 75°C – 100°C, the mass loss is suggested to be due to solvent volatilization from the Cu NPs paste that leads to a 16% weight decrease and a large decrease in resistance was also measured. This phenomenon was observed in Coutts *et al.* study as well [32]. In addition, a second and smaller decrease in weight occurring between 100°C – 200°C could be due to desorption of the remaining passivating layers that saw a <5 wt% lost in the TGA data. A slight drop in weight of approximately 0.4 wt% was observed after 200°C with further decrease in electrical resistance.

Though the thermal behavior of the Cu NPs can be studied via TGA, the study of microstructure evolution of Cu NPs during sintering might be difficult as fast cooling of TGA furnace is rather challenging due to equipment constraints. Since these Cu NPs are not electrically connected initially due to the presence of passivating layers, the sintering behavior of such passivating metallic NPs could be better studied through the change in electrical resistance during sintering.

Hence a method to relate the degree of contact (fusion) between Cu NPs in terms of a decrease in electrical resistance will be discussed in the following section.

4.2.1.1 In-situ Electrical Resistance Measurement

At the start of sintering, a high electrical resistance of the Cu NPs typically in the mega-ohm range is measured. This is due to the presence of the passivating organic materials that prevent the Cu NPs from forming percolated metallic networks. A schematic of a 2-particle illustration and FESEM image of un-fused Cu NPs is shown in Figure 4.3.

Figure 4.3 FESEM image and schematic illustration of Cu NPs before sintering

Assuming 2 spherical un-fused Cu NPs are in contact with each other, the total electrical resistance across the 2 Cu NPs, R_{Total} , can be divided into 3 parts, i.e. $R_{passivation}$, $R_{contact}$ and R_{Cu} . $R_{passivation}$ is dependent on the thickness of passivating layer while $R_{contact}$ is dependent on the contact area between the 2 Cu NPs and R_{Cu} is due to the Cu NPs itself.

When a drastic drop in weight occurred between 50°C – 100°C, a decrease in electrical resistance by 3 orders was observed (Figure 4.2). This change in electrical resistance is possibly caused by the volatilization of organic materials within the Cu NPs paste as measured by the TGA. Hence the total electrical resistance between 2 Cu NPs after volatilization can be represented as

$$R_{Total} = R_{Contact} + 2R_{Cu} \quad (4.1)$$

assuming all passivating layers are removed.

Here, the Cu NPs are assumed to be arranged in a regular manner (Figure 4.4) and are equal in size. The total electrical resistance for 1 layer of Cu NPs can be expressed as

$$R_1 = (n + 1)R_{\text{Contact}} + nR_{\text{Cu}} \quad (4.2)$$

where n is the number of Cu NPs in 1 layer.

Figure 4.4 Schematic illustration of the regularly arranged Cu NPs

The total resistance of the entire fused Cu NPs stack is assumed to be equivalent to the parallel resistance of individual Cu NPs layers. Therefore,

$$R_{\text{Total}} = \frac{(n + 1)R_{\text{Contact}} + nR_{\text{Cu}}}{d} \quad (4.3)$$

where d is the total number of layers within the fused Cu NPs stack.

However, during the onset and initial stage of neck growth, the contact resistance between 2 Cu NPs is assumed as one contact spot. When these Cu NPs touch one another over a small area, there is a constriction resistance between them as the electrical current flow within that small area is not a continuous flow, but

electrons will scatter off impurities and atomic defects in the conductor [33]. Therefore, the electronic collision mean free path, y , needs to be taken into consideration when developing the contact resistance model. When the radius of the constriction is equal to or less than the mean free path y , electrons will pass through the contact ballistically. To define the electronic conduction regime, Knudsen ratio $K = \frac{y}{X}$ is included in the calculation, where X is the radius of the constriction. Therefore, between classical and ballistic electronic conduction, the contact resistance, $R_{contact}$, across the small contact point between Cu NPs during the initial stage of neck formation after capping layers are removed can be expressed as [34, 35]

$$R_{Contact} = \tau(k) \underbrace{\frac{\rho}{2X}}_{\text{Classical}} + \underbrace{\frac{4\rho y}{3\pi X^2}}_{\text{Ballistic}} \quad (4.4)$$

where ρ is the resistivity of the bonded material, X is the contact radius, y is the electron mean free path, which Cu has a value of 38.7 nm at room temperature, K is the Knudsen ratio and $\tau(k)$ is a function decreasing from 1 to 0.694 as y/X increases from 0 to ∞ .

From Eqn. (4.4), consider that if the neck radius X is much smaller than the mean free path y , ($X \ll y$), the conduction will be dominated by ballistic transport.

Figure 4.5 FESEM image and schematic illustration of Cu NPs after volatilization and onset of neck growth at 150°C

As fusion of Cu NPs continues at higher temperature, the contact radius X increases due to surface and/or lattice diffusion from the NPs surfaces as shown schematically in Figure 4.6. Another drop in R_{Total} was measured from 150°C to 300°C (Figure 4.2) with further necking and growth of the NPs. The microstructure evolution of the Cu NPs during sintering will be shown and explained in Section 4.2.1.2.

Figure 4.6 FESEM image and schematic illustration of subsequent neck growth of Cu NPs and its agglomerated regions at 300°C when heated at 10°C/min

4.2.1.2 Particle growth and electrical resistance measurements

Since the change in electrical resistance is postulated to correlate with the different sintering stages of the Cu NPs, the microstructures of the Cu NPs at various stages can be captured and used for understanding the sintering behavior.

Using the FESEM images of Cu NPs taken at different stages of sintering, the size of the agglomerated region at various stages can be measured using image analysis method [19, 36]. When a significant change in resistance was observed *in-situ* during the sintering process, the sample would be cooled down rapidly to freeze the respective microstructure. The respective samples would then be analyzed using a FESEM and the micrographs would be used to measure the particle sizes at each stage. From the particle size curve shown in Figure 4.7, it can be seen that the Cu NPs grew exponentially with temperature and increased rapidly when the sintering temperature went beyond 230°C. Since heat flow increased and no change in weight was observed by DSC or TGA after about 230°C, it can be assumed that all the organic materials had been removed and fusing of Cu NPs occurred. Hence, the fused Cu NPs started to grow and further drop in resistance was observed.

Figure 4.7 Fused Cu NPs sizes as a function of temperature and the corresponding change in electrical resistance

Crossed-sectioned FESEM images of the microstructure evolution up to 300°C are shown in Figure 4.8(a). At the start of sintering, individual NPs of various sizes were observed. After the first drastic drop in both weight and electrical resistance is observed at about 120°C, most particles had yet to be fused. This is indicated by the Cu NPs remaining isolated, with little or no neck formation. The growth of these Cu NPs as charted in Figure 4.7 shows little or no increase in size from 25°C – 110°C. This agrees well with our previous explanation in Section 4.2.1.1 that the 15 wt% loss and 2 orders magnitude drop in electrical resistance were due to solvent volatilization. Subsequent heating (>150°C) would see significant neck formations and increase in particle sizes (Figure 4.7) as the passivating layers were desorbed and volatilized between 110°C – 230°C. This observation thus provides an explanation for the 5 orders magnitude drop in electrical resistance and a 3 wt% drop as indicated in Figure 4.2. As heating

Sintering and Densification Behavior of Nano-sized Copper Particles Chapter 4

proceeded beyond 230°C, rapid growth in particle size could be observed in Figure 4.7 and Figure 4.8(a). However, no drastic change in electrical resistance or weight is detected (Figure 4.2). This indicates that all or most of the organic materials had been volatilized by 230°C. Further small changes in resistance are due to further fusion and densification of these nanoparticles. However, after most of the Cu NPs have formed necking and majority of the organic materials were removed, the change in resistance is slower beyond 230°C. Based on all the data, a schematic diagram showing the overall sintering behavior of the Cu NPs is illustrated in Figure 4.8(b).

Figure 4.8 (a) FESEM images of microstructure evolution (Scale 500 nm), and (b) Schematic diagram of the Cu nanoparticles at different stages of sintering

4.2.2 Sintering Process of Cu NPs

From the above results, the fusion of these passivated Cu NPs requires the complete removal of the passivating organic layers prior to fusing. Upon fusion, the transition from an insulator to metal will lead to a significant decrease in electrical resistance. It is observed previously that the onset of fusion only occurs when the organic materials are volatilized. Hence any factor that can influence the temperature of volatilization of organic material, T_E , will eventually affect fusion temperature, T_F , and the final state of fusion i.e. degree of necking. It has been reported that the rate of desorption of passivating layers from the NPs surfaces is dependent on how good the interaction between the passivating ligands and surfaces that they are attached to [25]. In addition, when these ligands are desorbed, they need to be quickly removed away from the NPs to prevent re-deposition that could hinder subsequent fusion. Such fusion process, commonly termed as sintering, is a thermally activated process. Hence variables such as diffusivity and viscosity, which are temperature sensitive, can affect the rate of sintering.

Generally, polycrystalline materials are sintered by solid-state diffusional processes [37]. The entire sintering process of the Cu NPs can be generalized into three stages. The first stage, Stage 1, includes the removal of most organic materials and rearrangement of particles that follows the onset of neck growth between Cu NPs in Stage 2. During the neck growth stage, the sintering mechanism of the Cu NPs is considered to be due to surface diffusion as opposed to Oswald ripening for sintering of metallic NPs on a support, in which larger particles grow as the expense of smaller particles [38]. The signs of necking formed between adjacent Cu NPs that were heated up till 300°C as shown in Figure 4.8(a) could provide an indication that the sintering mechanism of these Cu NPs is dominated by surface diffusion since large amount of porosities were observed. Such surface diffusion is due to the high surface energy of these Cu NPs [26, 39]. Further studies and discussion on the dominant sintering mechanism will be presented in Section 4.2.2.5. While surface diffusion could have dominated in Stage 2, during Stage 3 when all or most of the organic materials are removed, these fused Cu NPs clusters grew rapidly as shown in

Figure 4.7. However, continuous fusion of these fused Cu NPs might be hindered by the increasing pore sizes between fused Cu NPs due to limited particle mobility [40]. Therefore, about 20% porosities were still observed after the sintering process. Detailed information on porosities will be discussed further in Chapter 5.

4.2.2.1 Relationship between T_E and T_F

Since there is a correlation between the changes in resistance and the sintering behavior of Cu NPs, a relationship between the onset temperature of volatilization, T_E and fusion temperature, T_F , can be established based on thermal and electrical analysis. From the DSC curve that is overlaid with the change in resistance measurement shown in Figure 4.9, two distinct endothermic peaks at 2 different volatilization temperatures are identified as T_{E1} and T_{E2} . These two temperatures are defined to be the midpoint transition temperature of the first and second endothermic peak corresponding to the volatilization of organic materials. On the other hand, fusion temperature T_{F1} and T_{F2} , located on the change in electrical resistance curve, are defined to be the first and second midpoint transition temperature of fusion, respectively. At T_{F1} , volatilization of the solvents has occurred and the NPs become electrically conductive as they become connected. Although the capping layer is still present, current can flow through as it is very thin and not completely insulating. At T_{F2} , volatilization of the capping materials occurs and the Cu NPs fuse to form more electrically conductive paths.

From Figure 4.9, it is shown that removal of organic materials was followed by a change in electrical resistance. After most of the passivating layers have been removed, the electrical resistance continues to drop due to fusion between Cu NPs. With this thermal and electrical data, it has demonstrated the feasibility of using such electrical resistance measurement technique to study the sintering behavior of passivated metallic nanoparticles during sintering.

Figure 4.9 Heat flow and change in electrical resistance of Cu NPs as a function of temperature

4.2.2.2 Relationship between Heating Rates and Volatilization

Since the sintering process of such passivated Cu NPs is heavily dependent on the degree and rate of removal of organic materials, presence of any remaining organic materials will hinder the subsequent fusing of Cu NPs to form a conducting metallic layer. Therefore, factors affecting the rate of volatilization need to be studied to achieve an optimal fused layer of conductive Cu NPs.

When the Cu NPs are subjected to a low heating rate, it will spend a longer time at the lower temperature regime. Hence the solvents will evaporate at a lower temperature regime, i.e. lower T_E . As heating rate increases, the NPs bypass the lower temperature regime faster and thus volatilization occurs at higher temperatures and this will cause an increase in T_E with increasing heating rate. Since volatilization is a kinetics reaction, it is dependent on both time and temperature [41].

From the TGA test results, *in-situ* electrical resistance measurements and FESEM images discussed in the previous section, it can be concluded that all

organic materials present need to be substantially removed to enable good fusion among these Cu NPs. Though these Cu NPs were sintered successfully at 200°C, nano-sized pores were still observed. It was reported that coarsening of Ag or Cu NPs without any passivating layers is controlled by surface diffusion from room temperature to about 150°C [13]. Since surface diffusion occurs at the lower temperature regime, the Cu NPs would have started fusing. Hence upon further heating, it will most likely not lead to much further densification of these fused Cu NPs as higher thermal energy is needed to further densify them since the effective radius of these fused Cu NPs has increased when compared to their initial radius [26, 42]. Hence, by increasing the heating rate, it will shorten the time spent at the lower temperature regime and increase T_E , which intuitively increases the onset temperature of fusion, T_F , subsequently. This helps to maintain the small effective radius of the NPs till its peak sintering temperature. Since the surface energy of these NPs is high, higher degree of densification can therefore take place at the peak sintering temperature (200°C) [26]. However, care needs to be taken as the removal of organic materials will be affected when the heating rate becomes too fast. Wang *et al.* [16] had reported partial sintering among NPs when these passivated Ag NPs were sintered directly at the peak processing temperature. As these Ag NPs were subjected to a high thermal energy at the start of sintering, it caused the organic materials to decompose or volatilized rapidly. When this happened, desorption of passivating layers and fusion of NPs would occur rapidly and non-uniformly. For organic materials near to open surfaces, they would be removed faster and caused rapid fusion of NPs that are located nearer to the surfaces. When the top layer fused faster than the bottom layer, it would close up the pores to the surface and thus prevent the escape of the remaining volatiles at the bottom of the Cu NPs layer. When this happens, it could potentially cause non-homogeneous sintering across the NPs, especially for thick layers. Hence a balance between removal of organic content and fusion of NPs needs to be established.

Since the fusion process of these organic passivated Cu NPs can be studied electrically, electrical resistance measurements were taken at different heating rates. Figure 4.10 shows the resistance curves of Cu NPs sintered at different heating rates from room temperature till 200°C under N₂.

From Figure 4.10, it is observed that there is an increase in the magnitude of final resistance of the sintered Cu NPs as heating rates increases. For heating rate of 7°C/min, a 5 order drop in electrical resistance was observed at the end of sintering compared to less than 1 order drop in electrical resistance for samples heated at 40°C/min to 200°C. The reason for the high electrical resistance is likely caused by the incomplete removal of the organic materials that prevented the dense fusion between the Cu NPs. Hence, FESEM images were taken at the end of each stage of sintering for different heating rates to analyze the microstructures and correlate with the change in electrical resistance. This will be discussed in the following Section 4.2.2.3.

Figure 4.10 *In situ* electrical resistance for Cu nanoparticles heated at different rates to 200°C

4.2.2.3 Microstructure evolution of Cu NPs at Different Heating Rates

At low heating rate of 7°C/min, it is observed that the electrical resistance started to drop at 90°C (T_{F1}) and 150°C (T_{F2}) (Figure 4.10). This shows that the removal of organic materials from the Cu NPs started at 90°C (Figure 4.11(a)). After the majority of organic materials were removed between 90°C to 150°C, the onset

of neck formation and growth between Cu NPs could lead to further decrease in the resistance. This phenomenon was also observed by Leite *et al.* [31]. It was reported that sintering, when done at a lower heating rate, would proceed in 2 stages. The first stage is the densification of agglomerates that will occur after solvent volatilization and in the second stage, the non-agglomerated particles will densify. After heating up to 200°C, though fusion among Cu NPs were observed, large pores were still present (Figure 4.11(a)).

As heating rate was raised to 17°C/min, T_{F1} and T_{F2} increased to 118°C and 180°C, respectively. From the microstructures images (Figure 4.11(b)), it is observed that after the first drop in resistance at 118°C, there was little or no fusion among Cu NPs unlike samples that were heated up at 7°C/min. This is because for the sample that was heated up at 17°C/min, it did not stay at the low temperature regime for extended period. Hence, significant fusion of Cu NPs after volatilization is not observed. At 180°C, an increase in particle size and sign of fusion were observed. In addition, it was observed that the Cu NPs that were sintered at 17°C/min has a denser microstructure with lower porosity after desorption of the passivating layers.

As heating rates was further increased to 30°C/min, it was observed that T_{F1} occurred at about 140°C. Further heating to 200°C led to further reduction in electrical resistance as desorption of remaining passivating layers and fusion of these Cu NPs proceeded. This demonstrates the possibility of achieving a denser microstructure by subjecting Cu NPs to higher heating rates that maintain a larger driving force for densification with smaller effective radius of the Cu NPs up to the peak sintering temperature of 200°C. However, it is observed from the FESEM images that there were still significant amount of porosities and unfused Cu NPs after heating up to 200°C. These observations were even more noticeable in high heating rate samples, i.e. 40°C/min (Figure 4.11(d)). This also provides an explanation on the high electrical resistance (observed throughout the sintering process (Figure 4.10) as there was little fusion among the Cu NPs. This phenomenon could be due to the short temperature ramp up time of about 5 minutes from room temperature to 200°C. Hence, it might not provide sufficient time for complete removal of the organic materials within the Cu NPs layer. Since large existence of un-fused Cu NPs might be the reason for the high

(>100 Ω) electrical resistance for higher heating rates samples, a longer annealing time at 200°C might lead to a further decrease in the resistance. Therefore, isothermal annealing at 200°C after the heating up cycle was carried out to promote further growth and densification of these Cu NPs that were heated up at different heating rates.

Figure 4.11 Microstructure changes of Cu sintered at (a) 7°C/min (b) 17°C/min (c) 30°C/min (d) 40°C/min (Scale: 500 nm)

4.2.2.4 Further Growth and Densification during Isothermal Annealing

After subjecting the Cu NPs at different heating rates to 200°C, we next investigate the change in electrical resistance and microstructure evolution with time as the atomic transport from the surfaces of Cu NPs to the neck is due to diffusion [26]. *In-situ* electrical resistance measurements were carried out to

relate subsequent fusion of Cu NPs with changes in electrical resistance during isothermal annealing. During the heating up process, after the organic materials were removed from the Cu NPs surfaces, the Cu NPs started to fuse. Based on the initial stage of sintering model as mentioned in Chapter 2, the general equation for neck growth, Eq. (2.1), can be used to describe the sintering mechanism. By rearranging Eq. (2.1) to express X in terms of m , n , H and t , it will be:

$$X = \left(\frac{H}{a^{m-n}}\right)t^{1/m} \quad (4.5)$$

where X is the radius of the neck formed between the particles, m , n are constants that depend on the sintering mechanism involved, a is the initial radius of the Cu NPs, H is a coefficient characteristic of the sintering mechanism and t is the time.

Eq. (4.5) can be used subsequently to relate the contact resistance to the neck radius during isothermal annealing.

As explained in Section 4.2.1.1, if the neck radius is smaller than the mean free path, y , R_c will be dominated by the ballistic electronic conduction. This means that the contact resistance, $R_{contact}$, that is dependently mostly on ballistic conduction during initial stage of sintering, can expressed in terms of the neck radius X as:

$$R_{Contact} = \frac{4\rho y}{3\pi X^2} \quad (4.6)$$

By combining Eq. (4.5) with Eq. (4.6) $R_{contact}$ can be expressed as,

$$R_{Contact} = \frac{4\rho y(a^{2m-2n})}{3\pi H^2 t^{2/m}}$$

(4.7)

Assuming no oxidation of Cu, the total resistance will be dominated by the contact resistances such that

$$R_{Total} \approx R_{contact}$$

From Eq. (4.3),

$$R_{Total} = \frac{(n + 1)R_{Contact}}{d} \quad (4.8)$$

Substituting Eq. (4.7) into Eq. (4.8)

$$R_{Total} = \frac{(n + 1) \frac{4\rho y(a^{2m-2n})}{3\pi H^2 t^{2/m}}}{d} \quad (4.9)$$

Simplifying Eqn. (4.9), the time dependence of the total resistance of the fused Cu NPs network can then be represented as

$$R_{Total} \propto t^{-2/m} \quad (4.10)$$

From Eq. (4.10), it is shown that the total resistance is related to the neck formation and growth of the NPs at constant temperature and the resistance follows the power law with time. We can therefore measure the electrical resistance of Cu NPs during isothermal annealing and determine the value m to suggest a possible sintering mechanism.

From Figure 4.12, the change in electrical resistance is very substantial during the first 5 – 10 minutes of isothermal annealing at 200°C. Based on the above explanation, this could indicate the fast transport of materials between Cu NPs

that led to neck formation and growth. However, it is observed that after 10 minutes of isothermal annealing, the rate of resistance change, represented by the slope of the curve, decreases. This is due to the decrease in driving force of the Cu NPs to further densify since they have grown bigger. Longer annealing time and/or higher temperature would be needed to further increase the fusion of the sintered Cu layer.

Figure 4.12 Resistance as a function of isothermal annealing duration for different heating rate samples

The microstructure evolution images of initial and subsequent fusion of these Cu NPs were analyzed and shown in Figure 4.13. At higher heating rates ($>7^{\circ}\text{C}/\text{min}$), the samples did not spend significant amount of time at the lower temperature regime during heating up, hence they were able to fuse and grow during isothermal annealing at 200°C . This translates to more neck formations and growth that led to the significant decrease in resistance observed. This is because the effective radius of the Cu NPs remained almost unchanged during heating up due to the short heating up time. On the other hand, for samples that were heated with a low heating rate of $7^{\circ}\text{C}/\text{min}$, it was observed that the drop in electrical resistance (Figure 4.12) and the microstructure evolution during

isothermal annealing (Figure 4.13(a)) are not significant. This can be explained that these Cu NPs had fused into bigger particles during heating up as they had longer exposure to the lower temperature regime. This increased their effective radius and caused them to lose their high surface energy to further densify at 200°C. When this happens, they will need a higher processing temperature, i.e. > 200°C, or external factors such as pressure for further growth and densification of these agglomerates. Since there is no further obvious increase in particle size and/or neck size, it is hypothesized that the paths available for electrons to flow remain relatively unchanged. Hence, minimum drop in electrical resistance was observed.

With the above observations, it can be concluded that a faster heating rate will be able to attain a denser layer since the samples will have a higher T_E and T_F . By observing the FESEM images of 17°C/min – 40°C /min samples shown in Figure 4.13(b) – (d), it is observed that as isothermal annealing time increases, the fused Cu NPs grew significantly for the first 5 – 20 minutes. This fusion and growth phenomenon was accompanied by 2 orders drop in magnitude of electrical resistance shown in Figure 4.12. Hence, it can be proven that the neck formation (fusing) is responsible for providing a pathway for electrons to flow that led to a drop in resistance. Beyond 20 minutes of isothermal annealing, no noticeable change in microstructures and electrical resistance was observed. It was reported by Kim *et al.* [14] that once necking was observed, a conductive film can be formed even though it is still porous but further densification will not have significant change in conductivity. This phenomenon is supported in Figure 4.12 that upon isothermal annealing for extended period of time (> 20 min), no significant change in electrical resistance is observed even though bigger fused Cu and large amount of pores were still present between 20 and 30 min. The final electrical resistances of samples were about 1 Ω for 7°C/min and 17°C/min, 9 Ω for 30°C/min and 200 Ω for 40°C/min. The high electrical resistance observed in higher heating rate samples, i.e. 40°C/min, might be due to the entrapment of organic materials since the presence of small and un-fused Cu NPs were still observable after 30 minutes of isothermal annealing shown in the FESEM images of 40°C/min sample (Figure 4.13(d)).

Figure 4.13 Microstructure evolution during isothermal annealing of Cu particles that were previously heated up at different heating rates (Scale bar in white: 500 nm)

4.2.2.5 Determining the Dominant Sintering Mechanism

Based on the electrical resistance measurements (Figure 4.12) and FESEM images (Figure 4.13), heating rates of 7°C/min and 17°C/min seem to have removed the passivating layers successfully during heating up for fusion to occur during isothermal annealing at 200°C. Hence to determine the dominant sintering mechanism, the change in resistance with time of the sintered Cu NPs that were heated to 200°C with a heating rate of 7°C/min and 17°C/min were used to determine the value of m .

(a)

Figure 4.14 Experimental results and proposed model prediction of resistance as a function of time (a) 7°C/min (b) 17°C/min

In Figure 4.14(a) for the sample heated at a rate of 7°C/min to 200°C, the decrease in electrical resistance is best fitted with $m = 7.2$ (red line) during the first 15 minutes of isothermal annealing, which is close to the value of 7 stated in Table 2.3 of Chapter 2 for surface diffusion. Beyond 15 minutes, the proposed model does not fit to the experimental results. This is because the proposed model assumes ballistic conduction as the dominating electronic conduction. Hence, a change in the dominant electronic conduction regime, i.e. from ballistic to classical, would affect the accuracy of the model. In addition, after prolonged sintering, the Cu NPs will fuse and causes shrinkage that causes discontinuity that could affect the resistance measurements since the Cu NPs paste is spread onto a self-made electrical test structure as shown in Figure 3.2. Another possible reason that the model does not match the actual resistance is that this model assumes minimum or no shrinkage of the sintered Cu NPs. Hence the ratio of $\left(\frac{X}{a}\right)$ is kept constant, assuming any change in neck size X is proportional to the particle size, a . However, as isothermal annealing proceeds further, sintering could transit to Stage 2 whereby densification occurs. Hence the particle size, a ,

changes and needs to be taken into consideration for the model as the ratio of $\left(\frac{x}{a}\right)$ will change to predict subsequent densification behavior.

From the FESEM images shown in Figure 4.13(a), the neck size grew with increasing isothermal duration, i.e. beyond 10 minutes, and less spherical Cu NPs was observed. Hence, it is reasonable to postulate that the deviation of the model after 15 minutes comes from the change in the proportion of ballistic conduction to classical conduction and the particle size.

On the other hand, for samples that were heated up at 17°C/min, the best fitted m value is 3.853. Therefore, according to Table 2.3 and Figure 2.6 (2), the dominating sintering mechanism could probably be lattice diffusion from the surface which is still considered as another form of surface diffusion since no densification was observed in Figure 4.13 (b). This is because unlike conventional lattice diffusion whose source of material during sintering comes from the grain boundary that eventually leads to densification, the source of material for such “lattice diffusion” comes from the surface. Hence it does not lead to densification. For this sample that was previously heated up at 17°C/min, the model is only able to predict up to the first 20 minutes of isothermal annealing as the model starts to deviate from the measured data eventually.

Figure 4.15 Experimental results and proposed model prediction of resistance as a function of time (a) 30°C/min (b) 40°C/min

Based on the model that was developed and the values of m and n calculated, when the heating rate was increased further to 30°C/min, the dominating sintering mechanism is lattice diffusion from grain boundary for samples that were heated up at 30°C/min (Figure 4.15(a)) when referred to the summarized values of the different sintering mechanism listed in Table 2.3 [43]. However, this is not true as lattice diffusion from grain boundary will lead to shrinkage, i.e. change in thickness and/or densification, and both are not observed in this study. In addition, from Figure 4.13(c), many un-fused Cu NPs were still present. For even higher heating rate of 40°C/min (Figure 4.15(b)), the fitting was poor with r^2 value of 0.69. Hence, the proposed model has failed to predict those higher heating rates samples as the sintering behavior could be more complicated.

The difference in sintering mechanism predicted by the model for samples heated at 7°C/min and 17°C/min could be attributed to the different T_E and T_F at different heating up rates. Since a higher heating rate will give a higher T_E that leads to a higher T_F , the effective radius of the Cu NPs is assumed to be small when it reaches the peak process temperature. Hence, when the Cu NPs are subjected to the maximum temperature without spending more time at the lower temperature regime, lattice diffusion from the surface can happen. On the other hand, if a low heating rate is used (7°C/min), the Cu NPs would have spent a longer duration at the lower temperature regime. Hence, surface diffusion which usually prevails at lower temperature due to its lower activation energy, would be the dominating mechanism.

With all these results from TGA, DSC, FESEM and *in-situ* electrical resistance measurements, a schematic model for this sintering process of Cu NPs is proposed. Based on the proposed schematic model shown in Figure 4.16, at optimized heating rate as depicted in Figure 4.16(a), the volatilization of solvent will occur first, follow by desorption of the passivating layers which subsequently lead to the fusion of Cu NPs. During isothermal annealing, the particles will continue to grow. A slightly porous yet low electrical resistance layer is thus formed.

Figure 4.16 Schematics diagram of Cu NPs microstructure evolution after (a) complete removal, (b) incomplete removal of organic materials.

On the other hand, if the heating rate is too fast ($>17^\circ\text{C}/\text{min}$) as shown in Figure 4.16(b), volatilization of solvent and desorption of passivating layers might be

incomplete. The organic materials that are trapped within the layer will lead to non-fusing or partial fusing of Cu NPs even after prolong isothermal annealing. This will eventually lead to a porous sintered Cu layer with high electrical resistance. Therefore, from the proposed schematic model, it highlights the importance of removing the organic materials completely. A slower heating rate might be one of the possible solutions. However, a higher sintering temperature is needed for further growth and densification due to the presence of agglomerates with larger effective radius that were formed during the slow heating up process. Therefore, the ability to completely remove the passivating layers from these Cu NPs surfaces fast to prevent partial and non-homogenous fusion will be explored in the next section.

4.2.3 Stability of Passivating Ligands under Acidic Environment

There are several factors that can increase the rate of desorption and volatilization of these passivating layers. These factors include providing a higher thermal energy to enhance desorption, increasing the flow rate of air to remove the volatiles quickly from the Cu NPs surfaces or introducing other gases to react with the passivating layers. As reported by Anto *et al.* [25], T_E is dependent on the thermal stability and packing density of the ligands on the particles' surfaces rather than the size of the nanoparticles. Since the amine ligands that were on the Cu NPs surfaces are able to volatilize below 200°C, they thus do not share strong bonds with the Cu NPs surfaces. Hence, by introducing a gas that can react with the passivating ligands and the by-products formed are able to volatilize readily to prevent redistribution, could enable better and faster removal of these passivating layers. This will effectively promote better fusion among Cu NPs.

Feeding N₂ gas into formic acid is a technique used to create a reduction atmosphere and it is also used in the industries for soldering applications (eutectic bonding) to prevent oxidation [44-46]. However, the main purpose of introducing formic acid vapor in our experiments is not to reduce copper oxide to copper. Its purpose here is to react with the amine ligands that are attached onto the Cu NPs surfaces. From the previous section, it is observed that the Cu

NPs that were used could be sintered at 300°C under N₂ with minimum presence of copper oxide. Figure 4.17 shows the XRD data of the as sintered Cu NPs film at 300°C. This proves that the reason for the high resistance measured and presence of un-fused Cu NPs especially at higher heating rates, is most likely caused by non-uniform removal of organic materials that led to poor fusion among Cu NPs.

Figure 4.17 XRD of sintered Cu NPs film at 300°C

Therefore, to improve the removal of the amine-based ligands from the Cu NPs surfaces, formic acid was used to understand the effectiveness of removing the passivating layers. In Figure 4.18, the *in-situ* electrical resistance as a function of time for Cu NPs sintered under N₂ and formic acid at a heating rate of 40°C/min shows a significant drop in resistance even during the short heating up period under formic acid environment.

Figure 4.18 *in situ* electrical resistance measurements during heat up at 40°C/min under N₂ and formic acid

From Figure 4.18, the rate of sintering under formic acid as represented by the rate of resistance change increases rapidly within the first 7 minutes of the sintering process, though heating up to peak temperature takes about 5 minutes. This shows that the reaction between formic acid and the amine-based passivating layer is possible even at low temperatures. The possible reaction between formic acid and the amine-based passivating layer is [27]:

With the reaction between formic acid and amines, it can form some by-products that volatilize readily, i.e. removed from the Cu NPs surfaces below 200°C. Hence it will allow fusion of the Cu NPs to occur rapidly due to the nano-size effect. Detailed chemical reactions between formic acid and the amine-based

ligands are beyond the scope of this study. Since these Cu NPs are not passivated anymore, they are not thermodynamically stable due to their high surface energy. In addition, the reduction of melting point for nanoparticles will enhance surface diffusion, thus reducing the onset temperature of fusion, T_F (Figure 4.19). The microstructure evolution of Cu NPs under conventional heating and formic acid vapor is shown in Figure 4.20.

Figure 4.19 Changes in T_F when HCOOH vapor is introduced with a heating rate of 40°C/min

Figure 4.20 Microstructure evolutions of Cu NPs (a) under conventional N_2 sintering profile (b) under high heating up rate with 18.125M HCOOH vapor (Scale bar: 500 nm)

From the resulting microstructures, fast removal of passivating layers leads to fast fusion among the NPs that resulted in the formation of highly interconnected string-like structures as shown in Figure 4.21(b). Larger particle sizes, with larger pores due to enhanced neck growth, which indicate better fusion, was observed for sample sintered under formic acid vapor. On the other hand, when passivating layers are removed slowly, the fused Cu looks “round” (Figure 4.21(a)). This observation is similar to what have been reported by Ristau *et al.* [47] where fast sintering of Au NPs using electron beam leads to string-like structure. However, for both conditions, the SEMs images do suggest that the same non-densifying mechanism had taken place since the porosity after sintering does looks similar. This shows that non-densifying mechanism is responsible for both sintering conditions since large amount of porosities were observed and sintering was done at a relative low temperature. However, for both conditions, the SEMs images do suggest that the same non-densifying mechanism had taken place since the porosity after sintering does looks similar. Nevertheless, the difference between fast sintering rate in formic acid is that the Cu NPs are well-connected while those that were sintered in N_2 still has some

Sintering and Densification Behavior of Nano-sized Copper Particles Chapter 4

small unfused Cu NPs. This is due to the non-uniform and slow removal of capping layers under N_2 . On the other hand, under formic acid, the passivation removal is fast since sintering (i.e. resistance drops) started to occur at 60°C . However, because the sintering temperature is low, only surface diffusion could occur which is a non-densifying mechanism as discussed in Chapter 2, that leads to high porosity of the Cu NPs after sintering.

Figure 4.21 Microstructure of Cu NPs sintered under (a) N_2 ($17^\circ\text{C}/\text{min}$) (b) 18.125M Formic Acid Vapor ($40^\circ\text{C}/\text{min}$)

As the final microstructures are very much different, μXRD was carried out to understand the grain orientation of the fused Cu NPs under different sintering environment. For Cu NPs that were sintered under N_2 (Figure 4.22(a)), no preferred grain orientations were observed as the relative intensities of all orientations were similar when sintered under N_2 with initial heating rate of $17^\circ\text{C}/\text{min}$ and annealed at 200°C for 10 minutes. On the other hand, when Cu

NPs were sintered under formic acid vapor (Figure 4.22(b)), a preferred grain orientation of (111) was observed though a much faster heating rate (40°C/min) was used. This phenomenon is believed to be due to the initial capping surfactants being more weakly bonded to the (111) orientation of Cu. Hence when formic acid vapor is used, these capping organic materials on the (111) surfaces will be the first to react with the formic acid vapor. This would cause fusion to start from this direction and eventually lead to a textured Cu formation. Such control growth direction by using surfactants to attach on a particular crystal orientation has been reported for controlled nanowires growth direction and shape [48, 49]. It has been suggested that capping surfactants in a particular direction could change a NP to grow into a nano-rod. This could also be the reason why the fused Cu NPs shown in Figure 4.21(b) appears to be elongated. With better grain orientation, it would translate to less grain boundaries that could explain the lower electrical resistance observed after sintering as well. This fast fusion between Cu NPs is made possible due to the reaction between formic acid and the amine-based passivating ligands that formed some by-products that can be decomposed or volatilized readily at low temperature. Thus a “clean” Cu NPs surfaces would be exposed to enable better and faster fusion to happen.

Figure 4.22 μ XRD for samples heated under (a) N₂ (b) Formic acid

Though some reports [44, 45] have stated the use of formic acid to reduce CuO from the Cu NPs surfaces to enhance fusion, the main role of formic acid in this study is to remove the amine-based passivating layers on the Cu NPs surfaces to promote better fusion among Cu NPs. Though there could be some reduction of

Sintering and Densification Behavior of Nano-sized Copper Particles Chapter 4

copper oxide (CuO) to Cu or even preventing the Cu from being oxidized when sintering, the main reason for poor fusion among Cu NPs is largely due to the presence of passivating layers since no obvious CuO peaks were detected for samples sintered under N₂ environment (Figure 4.21). Hence, the postulation made based on these findings is that the formic acid vapor reacts with the passivating ligands which were speculated to happen on the Cu NPs (111) direction and forms some volatile by-products that can be removed below 200°C. These by-products are able to evaporate away from the Cu without any redistribution. This exposes a “clean” Cu surface and allows fusion among these Cu NPs along this (111) direction. The removal of the by-product is critical because if it is not removed, the electrical resistance of the sintered Cu NPs will be affected. After ligand removal, the subsequent fusion of Cu will be driven thermodynamically by its size effect. From the combination of *in-situ* electrical resistance measurement, FESEM images and μ XRD data, it is possible to come up with an enhanced schematic diagram of the sintering process of Cu NPs under different environment as shown in Figure 4.23 assuming all passivating layers are removed completely.

Sintering behavior of Cu NPs

(a)

(b)

Figure 4.23 Schematic diagrams showing the sintering behavior under (a) N₂ and (b) Formic acid

However, bigger pores were observed when sintering was performed under formic acid due to low the T_E and T_F . Therefore, to achieve a denser microstructure, T_E and T_F have to be higher. Since from the previous data, the removal of passivating layers is slow under N₂, a 2-step sintering process under different environment can be considered. This means that only N₂ is introduced during fast heating up to prevent oxidation and minimize volatilization, followed by introducing formic acid vapor at the peak temperature to ensure that T_E and T_F are close together at the peak sintering temperature. This will allow the effective radius of the Cu NPs to remain small up till the peak sintering temperature. Further studies on this can be carried out in the future.

4.3 Conclusion

It is frequently reported that the processing temperature of NPs can be low due to its low melting point. However, in this study, this is not the main contributing factor for passivated metallic NPs but is due to the sintering mechanism. The onset temperature of sintering is more dependent on the removal of ligands that are attached onto the Cu NPs surfaces. In the first part of the study, a conventional sintering profile was designed based on the thermal properties derived from the TGA and DSC analysis. From these data, the Cu NPs displayed the possibility of fusion at 200°C. However, as heating rate increases beyond 17°C/min, minimum or no fusion among these Cu NPs occurs and high electrical resistance will be observed. The increase in heating rates increases T_E and T_F ,

which causes rapid volatilization and non-uniform fusion, especially for thicker Cu NPs layer. When this happens, there will be inhomogeneous removal of passivating layers as the volatility of the passivating layers is not as high. This subsequently affects the degree of fusion of these Cu NPs across the layer. A resistance-time model that is based on ballistic electronic conduction is proposed to estimate the dominant sintering mechanism of these Cu NPs held at constant temperature after the removal of the passivating layers. The stability of the passivating ligands on these Cu NPs surfaces can be lowered with the introduction of formic acid vapor. With the passivating layer removed effectively even at high heating up rates, these Cu NPs are able to fuse with a (111) preferred grain orientation at 200°C within a short period of time. A low resistance of about 0.1 Ω was achieved due to higher degree of fusion and better grain orientation. With all these results, a few conclusions can be made in this chapter.

- Complete removal of passivating layers is crucial for these Cu NPs to fuse and form a percolated network.
- A suitable heating rate must be designed to allow a balance between T_E and T_F . A higher T_E will lead to a delayed volatilization of the passivating layers, thus preventing fusion of NPs to occur at lower temperature. Therefore, if the passivating ligands are not very volatile, a fast heating rate will lead to non-homogenous fusion across layer due to non-uniform removal from the Cu NPs surfaces.
- A model based on ballistic electronic conduction at constant temperature was proposed to understand the initial sintering behavior and predicting the dominating sintering mechanism.

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Chapter 5

Influence of Sintering Parameters on Bond Strength of Cu NPs

As discussed in Chapter 4, it was concluded that the removal of the passivating layer is essential for fusing the Cu NPs at a low temperature of 200°C. This is because the degree of passivating layer removal prior to the Cu NPs fusion will eventually affect the final microstructure of the sintered Cu layer. It was concluded that the heating rate and sintering environment have a significant influence on the removal of the passivating layer on the Cu NPs. From the previous chapter, it was shown that the Cu NPs are well fused and have a low electrical resistance when they are sintered at 200°C. Therefore, in this chapter, these Cu NPs, which are in a paste-like form, are sandwiched between two Si chips that were sputtered with a thin layer of Cu. This structure will allow shear testing to be carried out and its bond strength to be quantified. The porosity, degree of necking between particles and sheared interface morphology from different sintering parameters will be studied based on the FESEM images of the fractured surface after shear test. A correlation between the final microstructure and bonding strength is then established. Isothermal annealing at 150°C in air was also carried out for 1000 hours to investigate the thermal stability of these Cu NPs bonded joint. Some degree of grain growth and a (111) texture were found after 1000 hours of ageing.

5.1 Introduction

In recent years, many researchers are investigating on metallic NPs for low temperature interconnections [1-4]. These metallic NPs have shown its ability to be sintered at a lower temperature, and yet upon fully sintered, possess properties that are similar to its bulk metals [5, 6]. Therefore, metallic NPs have been greatly studied as a viable alternative to replace high temperature Pb-based solder as a joining material [1, 4, 7]. The ability to process at a lower temperature provides an advantage of adopting the metallic NPs as a mainstream interconnection material as this means that during processing, the semiconducting devices could avoid initial die level stress and other possible circuit damages [8]. To date, many have reported using Ag or Au NPs as a bonding material [9-13]. Low temperature fusion of noble metal NPs for die attach is promising since they rely on the principle of atomic diffusion and consolidation rather than a change of state from solidus to liquidus [14]. In Bai *et al.* [15] work, they made a comparison between Ag NPs and Au80Sn20 solder. It was reported that the previous has a much lower calculated elastic modulus, i.e. 9 GPa, due to the presence of micro-pores in the sintered Ag NPs. This is an advantage over conventional high temperature solder as it is able to withstand the stress arising from thermal expansion mismatch during bonding. Though sintered Ag NPs has 2.4 times higher electrical resistivity than bulk Ag at room temperature, its electrical resistivity is still lower than current solder alloy [14].

In comparison with micron-sized Ag particles, these Ag NPs can be fused at a much lower pressure, i.e. 1 – 5 MPa, while keeping the same processing temperature as micron sized Ag particles. This pressure range is definitely much lower than the 9 – 40 MPa used during bonding of micron-sized Ag particles [16]. This decrease in bonding pressure is attributed to the higher surface energies due to the size of the NPs [14].

However, Ag NPs often incurred higher cost and are subjected to ion migration [17]. Hence the next alternative is to look into Cu NPs as Cu also possesses high electrical conductivity and has strong durability towards ion migration and it is lower in cost [8, 17]. Though previous studies on the bondability of Cu NPs have been carried out, they were either done at a much higher temperature, i.e. 230°C

and above or under vacuum and forming gas environment [8, 18-20]. Such processing techniques will incur higher operational costs and is not suitable for polymeric substrates. In addition, there is a lack in understanding about the relationship between microstructures and mechanical properties that arises from different sintering parameters. Fu *et al.* [3] had stated that the sintering temperature, annealing time and heating rate has a direct influence on the pore size and pore distribution, which eventually affect the overall shear strength.

Therefore, this chapter aims to study the microstructure of the sintered Cu in detail and specifically its relationship with the mechanical properties. The first half of this chapter will discuss the effects of various sintering parameters on the shear strength of sintered Cu NPs bonded between 2 sputtered Cu layers. The fusion mechanism, degree of neck growth and porosity will also be looked into. After which, the stability of the sintered Cu NPs joints will be studied in terms of degree of grain growth and preferred texture after thermal annealing under air condition for 1000 hours.

5.2 Experimental Method

5.2.1 Bonding and characterizations of fused Cu NPs

Various heating rate (7 – 40°C/min), different isothermal annealing duration (5 – 30 minutes) at 200 – 300°C, bonding pressure ranging from 0 – 5 MPa and nitrogen or formic acid environment were studied on their impact on Cu NPs bonding. Correlation between all these bonding parameters with the joint strength will be studied. The mechanical shear strength of the bonded joint was characterized with a die shear test. To achieve statistically reliable results, 6 measurements were taken for each data point. After shear test, the cross-sectioned of the sheared surfaces were characterized using FESEM and the percentage of porosity of the fused Cu after bonding with applied pressure was calculated using ImageJ software from the obtained images. The grain sizes evolution and texture of the aged Cu NPs after isothermal ageing test were studied using synchrotron radiation μ XRD diffraction patterns.

5.3 Effects of Bonding Parameters

5.3.1 Effect of Heating Rate

In Chapter 4, a heating rate between $7^{\circ}\text{C}/\text{min}$ – $17^{\circ}\text{C}/\text{min}$ was deemed to be an appropriate heating rate for fusing these Cu NPs. However as compared to the previous chapter, the focus of this chapter is targeted towards bonding applications. This means that the Cu NPs paste is sandwiched between two Si chips that have been sputtered with a 500 nm thick Cu film. As fusion of the Cu NPs is heavily dependent on the removal of the organic materials, a covered structure will pose some additional challenges to the removal of organic materials due to confined space [12]. The path available for volatilization will be less as compared to an uncovered structure. Hence the rate of volatilization is postulated to be slower than an open structure, and this in turn might affect the degree of fusion among Cu NPs if they are sintered under the same conditions as stated in Chapter 4. The different pathways for volatilizations under covered and uncovered structure are schematically presented in Figure 5.1.

Figure 5.1 Schematic diagram of how the passivating layers on the Cu NPs escape under (a) covered and (b) uncovered structure

Since the volatilization may be more challenging under a covered structure, the optimum heating rate needs to be re-investigated. Prior to bonding, the microstructure of an un-sintered Cu NPs layer was characterized using FESEM coupled with FIB milling capability. This is to analyze the microstructure evolution of these covered Cu NPs before and after bonding at different heating rates. Small, individual and un-fused Cu NPs were observed as shown in Figure 5.2(a). The black regions that are shown in Figure 5.2(b) indicate the presence of organic materials before bonding. A zoom-in image of the joint layer, Figure 5.2(c), shows that there were different sizes of Cu NPs and no sign of necking

among them. This indicates the effectiveness of the passivating layers in preventing spontaneous fusion of Cu NPs under ambient condition.

Figure 5.2 FESEM images of un-sintered Cu NPs. (a) Top view, (b) Cross sectioned and (c) Zoom in of the bonded layer

After bonding and shear testing, the shear strength of the sintered Cu joint and its corresponding microstructure from each heating rate are presented in Figure 5.3 and Figure 5.4, respectively.

Figure 5.3 Shear strength of sintered Cu NPs joints at different heating rate

Top View

Cross-sectioned

Figure 5.4 Microstructure of Cu NPs joint at ramping rate of (a) 7°C/min (b) 17°C/min (c) 30°C/min (d) 40°C/min (Scale Bar: 500 nm)

A comparison between heating rate and shear strength shows that shear strength increases with increasing heating rate up till 17°C/min. However, as the heating rate increases beyond 17°C/min, the shear strength of the sintered Cu joint starts to drop. Further examination on the microstructure (Figure 5.4(c) and (d)), indicates that as the heating rate increases to 30°C/min and beyond, there is little

or no fusion among some Cu NPs. This could perhaps be caused by incomplete removal and/or trapping of the organic materials within the Cu NPs layer due to shorter total cycle time and confined space. Though fast heating rate promotes denser structure due to minimization of aggregation during the heating up stage, it was reported that unstable volatilization at higher heating rates during bonding can cause cracks within the layer and weaken the joint strength [8, 12]. Hence the rate of heating used should allow sufficient time for the removal of organic materials that leads to subsequent fusion yet minimize the formation of cracks within the layer that could affect the shear strength [21]. Since the presence of organic materials will impede NPs from fusing and thus affect densification, it will be particularly more critical for the covered structure to have a suitable heating rate that allows complete volatilization of organic materials and fusion of Cu NPs within a reasonable cycle time. In our study, we have observed that more necking, growth and densification of Cu NPs for samples bonded at 7°C/min and 17°C/min (Figure 5.4(a) and (b)) as compared to the higher heating rate samples (Figure 5.4(c) and (d)). However, if the heating rate was 7°C/min, after the passivating layers on the Cu NPs have volatilized at the lower temperature regime (<150°C), these Cu NPs would start to fuse due to their high surface energy. It was reported that the coarsening of un-passivated Ag or Cu NPs is dominated by surface diffusion mechanism from room temperature to around 150°C [9, 22]. Since the removal of these passivating layers leads to fusion of the NPs, the onset temperature of volatilization of solvent and desorption of passivating layers is crucial. A lower onset temperature of volatilization and desorption of passivating layers will lead to the earlier removal of organic material and fusion to happen at the lower temperature regime, which leads to surface diffusion which was observed in Chapter 4. This is deemed undesirable as surface diffusion does not contribute to densification [23]. Hence, to enable further growth and densification, a higher thermal energy will be needed, i.e. >200°C. This is proven from the microstructural images of samples heated at 7°C/min and 17°C/min shown in Figure 5.4(a) and Figure 5.4(b). The average size of the fused Cu for 7°C/min sample, Figure 5.4(a), is smaller than that of 17°C/min sample (Figure 5.4(b)) though the total cycle time for sample heated at 7°C/min is 15 minutes longer. The presence of unfused Cu NPs observed in 7°C/min samples may provide a possible explanation on the lower

shear strength attained. With these results, it is noted that a heating rate of $17^{\circ}\text{C}/\text{min}$ is more suitable for the Cu NPs to be fused under covered structure. Such a heating rate is able to provide sufficient time for the removal of organic materials and yet at the same time able to keep the effective radius of the Cu NPs small up till the peak bonding temperature of 200°C for good fusion and densification.

5.3.2 Effect of Bonding Temperature

The fusion between these Cu NPs is dependent on the removal of the passivating layers. Subsequently when these passivating layers are removed, the onset of fusion will occur. From Chapter 4, it was suggested that the sintering mechanism is dominated by surface diffusion. Since both removal of passivating layers and fusion of Cu NPs are temperature dependent, a temperature higher than 200°C would increase the bond integrity. Hence, the mechanistic change in bond formation at different temperatures, its bond integrity and final microstructure will be investigated in this section.

Figure 5.5 shows the different microstructures of Cu NPs bonded at different temperatures. It is observed that the Cu NPs size and necking among particles increase with increasing temperature and time. Intuitively, a higher temperature will accelerate diffusion since it has an Arrhenius relationship, leading to more necking and bigger fused particles. With better fusion and bigger particle size, it would give a denser sintered layer that result in a higher bonding strength.

Figure 5.5 Microstructures evolution of Cu NPs bonded at (a) 200°C (b) 250°C (c) 300°C for 0 – 20 min (scale bar: 1 µm)

The shear strength of the bonded samples from different bonding temperature was measured as shown in Figure 5.6. In addition, the average porosities were calculated based on the FESEM images shown in Figure 5.5. The cross-section image of each sample was taken and binarized using imaging software, ImageJ, which would make the Cu NPs appear black and pores as white. The porosities were then calculated using the particle analysis function found within ImageJ. To calculate the porosity of each condition, an average of 3 cross-sectioned SEM images were taken from each sample and plotted in Figure 5.7.

Figure 5.6 Shear Strength as a function of isothermal duration at 200°C, 250°C and 300°C

Figure 5.7 Porosity of Cu NPs layer with respect to time for samples bonded at 200°C, 250°C and 300°C

From the bond strength and porosity results, there are 2 major observations. When bonding is done at higher temperature, the bond strength increases faster with increasing bonding time. This rate of improvement is represented by the slope of the curve shown in Figure 5.6. This trend was also observed in Nichting *et. al.* [24] study whereby for low processing temperature ($<200^{\circ}\text{C}$), prolong annealing does not have significant improvement to bond integrity.

To correlate porosity with shear strength, it is observed that the change in percentage of porosity with time across these three temperatures is very different as well. For samples bonded at 250°C and 300°C , the amount of porosity decreases with time due to densification which could explain the increase in shear strength. However, the changes in porosity with time for the 200°C samples were small. This could be due to the lower bonding temperature that is insufficient for densification mechanism to take place. This again proves that prolong isothermal annealing for low temperature bonding is not as effective as high temperature ($>200^{\circ}\text{C}$) bonding.

However, care has to be taken when correlating porosity with shear strength. This is because when the Cu NPs were sintered at 300°C , it has the highest amount of porosity at the start of isothermal annealing. However, it also accounts for the highest bond strength (~ 6 MPa) as compared to the Cu NPs sintered below 300°C . Such observation can be explained from the microstructures as shown in Figure 5.5. Though 300°C has the highest percentage of porosity, the neck size and amount of necking in the sintered Cu NPs was also bigger and higher. Though the porosity of samples sintered at 200°C was close to the samples sintered at 250°C , small spherical Cu NPs with minimum necking were observed up till 15 minutes of isothermal annealing. Hence this resulted in a lower bond strength for samples sintered at 200°C . These results show that using the amount of porosity to correlate with shear strength can be very misleading if the degree and number of necking across sintered layer is not taken into consideration when comparison is made.

5.3.3 Effect of Applied Pressure

Though with the increase in bonding temperature can lead to better bond integrity, low temperature bonding is still very much preferable as some

substrates are temperature sensitive and a lower processing temperature is more economical. Many studies have reported that the addition of pressure could help to break down the organic layers on the NPs locally. This increases the number of contact points among adjacent particles and bonding interface for better fusion that eventually leads to a denser structure with a better joint strength since the total contact area has increased [11, 21, 25]. This is schematically represented in Figure 5.8. With the introduction of pressure, it helps to increase the sintering rate as materials are brought closer which increases the number of pathways and reducing the distance for atomic diffusion and thus increases the overall driving force for sintering [11, 26, 27]. Thus, sintering of these NPs can be done with a lower thermal budget. In order to make this applied pressure the critical factor affecting NPs fusion, it has to be larger than the intrinsic pressure within the material itself. This intrinsic pressure is dependent on the particle size. It has been reported that there is an increasing contribution from the surface curvature as the particle gets smaller. This could provide an explanation for the lower bonding pressure needed for NPs sintering as compared to micro-sized powder sintering [28].

Figure 5.8 Schematic diagram of bonding without and with bonding pressure exerted

Based on Mo *et al.* [29] study, a linear relationship between contact area and joint strength exists which determines the bond integrity. Such a relation can be represented as

$$F = kA_c \quad (5.1)$$

where F is the joint strength, k is the proportional constant and A_c is the contact area.

Assuming that all organic materials are removed and the surfaces of Cu NPs are free of oxide and other impurities, the increase in neck formation and growth when a bonding load is applied will bring these Cu NPs closer to one another for better diffusion. This will lead to some material deformation that can increase the contact area and thus result in joint strength improvement [11, 30].

Under a constant load during bonding, the duration of bonding and the amount of pressure exerted could allow these Cu NPs to come into contact with one another or with the bonding substrate. The overall increase in contact area can be due to diffusional mechanism or creep deformation if the pressure exerted exceeds the intrinsic pressure of the Cu NPs.

Figure 5.9 Schematic diagram of deformation between Cu NPs

As shown schematically in Figure 5.9, when the applied pressure did not exceed the intrinsic pressure, the contact area between bonding surface would not be maximized as it would be purely driven by Van der Waals force as marked by x in Figure 5.9. Hence, any increase in contact area is purely due to diffusional mechanism and the amount of atoms taking part in the diffusion process could be low. However, when bonding pressure is introduced or increased, the amount of deformation, w , will increase and when w has reached or has gone beyond the critical deformation, termed as w_c , some form of deformation is observed and an increase in contact area has resulted. This will increase the number of atoms taking part in the diffusion process and at the same time increases the rate of diffusion.

From the above explanation, such deformation of the Cu NPs at the bonding interfaces and between Cu NPs can also increase the van der Waals force between bonding surfaces as the distance between Cu NPs and bonding substrate is now closer. As reported by Joo *et. al* [31], one of the factors that cause particle adhesion through van der Waals forces is the distance between bonding surfaces. Hence by introducing some bonding pressure, these Cu NPs are brought closer towards the surface of the bonding substrate and other Cu NPs which therefore

helps to enhance adhesion through the increase in van der Waals forces. In addition, the shorter distance between bonding surfaces can also increase the possibility of diffusion interfacial reaction as explained in Chapter 4. As bonding pressure and time increase further, the amount of deformation as illustrated in Figure 5.9, w , will increase. When this deformation goes beyond the critical deformation, termed as w_c , some form of deformation can be observed. Hence there could be a change from initial diffusional mechanism to creep deformation when external pressure is exerted [32]. It is reported that for metals, power-law creep is usually the dominant densification mechanism when external pressure is used during sintering [33]. This eventually can help to improve the overall joint integrity since the overall contact area of bonding surfaces have increased.

Hence, experimental studies were carried out in this section to study the effect of bonding pressure on the joint strength and to find out the dominant sintering mechanism (diffusional or creep) under different bonding pressure. These samples were bonded with a bonding pressure between 0 – 5 MPa and held isotherm at 200°C for 0 – 20 minutes. It is observed that these Cu NPs will self-fuse even without application of any bonding pressure due to the high surface energy that comes from the surface curvature and van der Waals forces between Cu NPs and substrate that increases surface diffusion (Figure 5.10). However, the failure location of these pressureless bonded samples during shear test occurs mainly at the bonding interfaces. In addition, the contact between fused Cu NPs and the bonding interfaces were weak leading to adhesive failure. Figure 5.10 shows that by adding a relatively low bonding pressure of 1 MPa, it will cause the average shear strength to increase by more than 100% as compared to pressureless bonding. This improvement in strength could possibly be due to two reasons. One is that when pressure is added, it can help to break down the passivation layers and aid the physical desorption of these passivating layer from the Cu NPs surfaces during fusion [26]. When this happened, these organic materials are detached from the Cu NPs surfaces to enable fusion among Cu NPs to occur. The second possible reason could be the exertion of pressure during bonding increases the number of contact areas among adjacent Cu NPs and Cu NPs/bonding surfaces as it brings the Cu NPs and bonding surfaces closer to one another to enhance diffusion. The thickness of the joint was also reduced and the

spread of Cu NPs was more even due to the introduction of pressure during bonding. This could eventually help to form stronger bonds as the removal of organic layer is easier for thinner joint and the wettability between chip and substrate has improved. In addition, it was reported that the shear strain induced by bonding pressure tends to aid in the rearrangement of the NPs to form a denser structure, better grain alignment and minimizes the size of the pores formed [26]. However, no sign of ductile failure was observed on the fracture surfaces for samples that were bonded with a pressure between 1– 3 MPa though an increase in shear strength was observed (Figure 5.11(a) – (c)). This means that the increase in shear strength could just be attributed to diffusional dominated mechanism with no plastic deformation. On the contrary, as pressure increases to 5 MPa, sign of plastic deformation as shown in the corresponding microstructures in Figure 5.11(d) was observed on the failure surface. In addition, from the microstructural images shown in Figure 5.11, it is noted that as pressure increases, the layer did become more densified i.e. less porous. However, plastic deformation on the Cu NPs failure surfaces was only observed when 5 MPa of pressure was added (Figure 5.11(d)). This could mean that the deformation, w has gone beyond the critical deformation, w_c and a combination of diffusional fusion and plastic deformation could have taken place and increases the contact area between Cu NPs to improve the bonding at the interfaces and between Cu NPs. A handful of researchers had reported that with the formation of such dimple-like morphology, it would result in higher bonding strength as it indicates ductile failure which was torn off by shear stress [1, 4, 34]. Therefore, a minimum bonding pressure of 5 MPa is needed to overcome the intrinsic pressure of the Cu NPs for stronger joints.

From the FESEM images of both the failure surface and cross-sectional area, all the Cu NPs had fused well (Figure 5.11). Hence porosity comparison can be done across these samples. To quantify the amount of porosity, the percentage of porosity was again calculated using imaging technique. Cross-sectioned FESEM images of the sheared samples from different bonding pressure were used. The black regions shown in the FESEM images were taken to be the porosities of the sintered layer. Therefore, from the porosity percentage curve shown in Figure 5.10, an inverse relationship between shear strength and

porosity was observed. A lower percentage of porosity will see a higher shear strength as the degree of densification of the sintered layer is deemed to be higher. Hence with the introduction of an external pressure, it might be able to bring these Cu NPs and bonding surfaces closer to one another for better fusion during bonding.

Figure 5.10 Relationship between shear strength and porosity as a function of bonding pressure

Figure 5.11 FESEM images of fracture surfaces and cross sectioned of sintered Cu joints at (a) 0 MPa (b) 1 MPa (c) 3 MPa (d) 5 MPa (Scale bar of 500 nm)

With the introduction of a small amount of pressure ($\sim 1 - 5$ MPa), it is also observed that the improvement in shear strength can be due to better bonding between Cu NPs and the bonding surfaces. When pressure is applied, it is sufficient to bring the Cu NPs closer, thus increases the number of contact points

or area between Cu NPs for better diffusion. If the pressure exerted exceeds the threshold stress, further material deformation will increase the contact area. Cross-sectioned FESEM images of the sintered Cu layer with the bonding interface (with and without pressure) are shown in Figure 5.12. It is observed that the number of voids between sintered Cu NPs and bonding interface decreases with the introduction of pressure, which changes the failure mode to cohesive failure.

Figure 5.12 Cross-sectioned FESEM images of sintered Cu with and without pressure

Though 5 MPa seems to be the threshold pressure that could effectively cause plastic deformation of Cu NPs and enhance joint integrity, it is also dependent on the bonding temperature, density of Cu NPs, type of passivation layers used and size of the Cu NPs.

5.3.4 Effect of Bonding Environment

Though the application of pressure can produce a stronger bonded joint at 200°C, pressureless bonding may still be preferred in certain applications. Hence, based on the data gathered in previous sections, the rate and effectiveness in removing the passivating layers remains the key determining factor for joint integrity.

Based on the results gathered in Chapter 4, it was established that the removal of passivating layers is fast and effective under formic acid vapor as compared to under N₂ environment. In addition, a higher heating rate is good as it

minimizes aggregation of the Cu NPs during the temperature ramp up stage, hence densification would only occur at the peak bonding temperature. Based on this knowledge, a heating rate of 40°C/min was chosen and introduction of formic acid vapor only at the peak bonding temperature of 200°C was designed.

In Figure 5.13, it is observed that the shear strength of the bonded joint increases by threefold when bonding was done under formic acid vapor environment. A closer look at the corresponding microstructures in Figure 5.14 shows that the Cu NPs are well-fused though a higher heating rate of 40°C/min was used, and the total process time was only 14 minutes.

Figure 5.13 Shear Strength of Cu NPs joint under N₂ and Formic Acid

Figure 5.14 Microstructures of the sintered Cu NPs under (a) N_2 and (b) formic acid vapor

To explain the significant improvement in joint strength, *in-situ* electrical resistance measurement was deployed to understand the fusion mechanism as adopted in section 4.2.1.2 (Figure 5.15).

Figure 5.15 *in-situ* Electrical resistance measurements under N₂ and formic acid vapor environment whereby isothermal annealing is done at 200°C

It is observed that the change in resistance under formic acid is very rapid after 6 minutes of isothermal annealing and its final resistance is in the ohm-range. As discussed in section 4.2.1.2, the removal of the passivating layer under formic acid is faster since it is a chemical reaction between formic acid vapor and the amine-based passivating layer. However, for samples that were bonded under N₂ environment, the rate of change is slower as the removal of passivating layer is solely dependent on the volatilization process. Hence complete removal of passivating layers might not be possible and hence results in a higher final resistance. From the previous study, it is concluded that the high resistance is due to poor fusion between Cu NPs and is caused by the remaining passivating layers. This again shows that the rate and degree of passivating layer removal is critical for good fusion of Cu NPs to achieve a high bond integrity with low electrical resistance.

In the data presented above, the purpose of using the formic acid vapour is for more effective removal of the capping layer, and not for reduction of any pre-existing copper oxide or prevention of copper oxidation. If the capping layer is removed effectively, it can allow the Cu NPs to be sintered at a much lower temperature and even lead to a textured growth of the Cu grains. Nevertheless, based on the author's knowledge, the use of formic acid might not be conventional in the current manufacturing process.

Therefore, we can envisage that by tuning the chemistry of the Cu NPs paste formulation through having a component with similar characteristics as the formic acid that could be activated upon heating to react with the capping layers to volatilize them, fusion of the Cu NPs can take place without the use of formic acid vapor.

5.3.5 Relationship between Microstructure, Porosity and Bond Strength

From the above findings, the porosity of the bonded Cu NPs layer is dependent on bonding parameters such as heating rate, bonding temperature, applied pressure and bonding environment. A good bond, which is known to have a higher true contact area [35, 36], is defined in this thesis as having high contact area at the bonding interfaces with the chip/substrate and strong bonding among the Cu NPs within the bonded layer. The amount of porosity might not be closely related with the mechanical strength if the bonding among Cu NPs, and between Cu NPs and bonding interface is not strong, i.e. significant amount of neck growth between Cu NPs and at the interface.

It is observed that when bonding was done at a lower temperature, i.e. 200°C, introducing pressure does help to increase the true contact area due to diffusional mechanism and creep deformation between Cu NPs. This increases the amount and degree of necking that leads to an increase in bond strength. As shown schematically in Figure 5.16(a), when bonding is done at 200°C without any pressure and for a short duration (i.e. ~10 minutes), the non-uniform volatilization of passivating layers would lead to poor fusion. Hence, most of the Cu NPs remain small and are attracted toward one another by weak forces such as Van der Waals forces (Figure 5.16(b)). However as bonding temperature increases beyond 200°C or when pressure is exerted, the degree of necking

increases which increases the contact area, and thus the joint strength of the Cu NPs layer is enhanced.

Therefore, the type of bonding of the Cu NPs affects how the joint fails. When cracks occur among the Cu NPs agglomerates, they are able to propagate along the Cu NPs easily when they are bonded by weak forces. On the other hand, if the Cu NPs are bonded together by solid necks, though higher porosity is observed, the resultant bond strength will be higher. This higher bond strength is attributed to the strong metallic bonds made between these Cu NPs through the fusion and necking process. Hence from this result, it shows that though shear strength is a function of the contact area, the true contact area between the NPs from the solid-state bonding is the critical parameter. The degree of neck growth across different samples has to be taken into consideration rather than taking porosity as a simple estimation of bond integrity. This is to ensure that the type of bonding between sintered Cu NPs is similar (van de Waals forces vs. solid neck formation) before further comparison and studies are done.

Figure 5.16 Schematics illustration of densification at (a) 200°C and (b) 300°C
(Scale bar: 1 µm)

With different types of bonding occurring between Cu NPs after fusion, two different types of failure were proposed. Type 1 failure is defined in this thesis as failure along the weakly bonded Cu NPs whereas Type 2 failure refers to failure occurring between the Cu NPs that are strongly bonded by solid necks (Figure 5.17). Hence when relating the relationship between shear strength and porosity, it must be compared against similar failure type. If the comparisons were not done according to the type of failure, the true contact area theory will not hold. This has been shown in Figure 5.6 and Figure 5.7. Though a lower or similar amount of porosity was observed in 200°C bonded samples as compared to 300°C ones, higher bond strength was observed in the latter. From the FESEM images (Figure 5.16), the type of failure in 200°C samples is most likely to be Type 1. Whereas for 300°C samples, Type 2 will be more dominant. Therefore, the amount of porosity does not always correlate with the bond strength unless comparison is done across samples with the same type of failure.

Figure 5.17 Failure types and locations (a) Type 1: Propagate along weakly bonded Cu NPs (b) Type 2: Does not propagate easily along Cu NPs due to strong bonding

5.4 Bonded Cu NPs stability over time

To study the thermal stability of these sintered Cu joints, isothermal ageing test at 150°C under air condition was done on these samples for up to 1000 hours. At every 200 hours, 6 samples were removed from the furnace for shear testing, cross-sectional FESEM imaging and synchrotron XRD characterization to characterize the bond strength, microstructure and grain growth of the aged samples.

5.4.1 Bond strength

5 samples were taken for shearing at every 200 hours interval and the shear strengths are shown in Figure 5.18.

Figure 5.18 Shear strength of sintered Cu NPs under isothermal ageing at 150°C for 1000 hours

Influence of Sintering Parameters of Cu NPs & its Structure Stability Chapter 5

From the results, the shear strength of the bonded samples increased significantly (~3 times) for the first 200 hours. This drastic improvement can be correlated with the microstructure of the sintered Cu NPs. From the microstructure evolution from 0 – 1000 hours (Figure 5.19), it is observed that the porosity of the bonded layer has decreased tremendously for the first 200 hours. This would cause the increment in shear strength as the Cu NPs are better fused, and a denser bonded layer has been formed. An overall increase in shear strength was observed throughout the ageing process. However, no significant change was observed from the microstructures after 200 hours though there is an increase in shear strength. This could mean that grain growth of these Cu NPs could have affected the shear strength. To verify if any grain growth or crystallographic texture changes of the Cu NPs had occurred during the isothermal ageing process, synchrotron micro X-ray diffraction analysis (μ XRD) was used.

Figure 5.19 Microstructure evolutions of bonded Cu layers during ageing test from 0 — 1000 hours (Scale bar: 500 nm) The red dotted lines indicates highly fused Cu particles after 1000 hours of isothermal ageing

5.4.2 Synchrotron μ XRD

The as-sintered and aged samples show four peaks at 2θ values of 28.971° , 33.511° , 48.059° and 56.959° , corresponding to (111), (200), (220) and (311) planes of copper. The relative intensities of the first 3 orientations, (111), (200) and (220), are tabulated in Table 5.1. Relative intensities were calculated from the intensity of a peak divided by the intensity of the 'strongest' peak. Each relative intensity is an average of 3 scan areas.

Table 5.1 Relative intensity of aged Cu NPs

Time (hours)	Relative Intensity (%)		
	(111)	(200)	(220)
0	100	83.072	61.77
200	100	71.56	44.31
400	100	60.56	41.98
600	100	40.87	37.54
800	100	34.89	32.69
1000	100	25.68	35.31

From Table 5.1, there is no strong preferred orientation before isothermal ageing as the relative intensities are similar. This could be due to the short total processing time of 10 minutes at 200°C as crystallite growth is a function of time and temperature. However, after ageing for 1000 hours, the preferred growth orientation is (111) as the relative intensity as compared to (200) and (220) is much higher. In addition, as ageing proceeded, the intensities of both (200) and (220) decreased. This means that the volume fraction of (111) crystallites has increased with ageing time and is speculated to be due to grain rotation. The XRD patterns of the fused Cu NPs before and after 1000 hours of isothermal annealing are shown in Figure 5.20.

Figure 5.20 XRD patterns of Cu NPs (a) before (b) after ageing for 1000 hours

5.4.2.1 Relationship of Shear strength with (111) FWHM

Scherrer *et al.* showed that when the particle size of a randomly orientated mass of crystal is small, the beam of the parallel monochromatic radiation that falls onto the crystal will be broaden [37]. Therefore, the crystallite size along the d -spacing direction of a peak is closely related to the full-width-at-half-maximum (FWHM) of a specific diffraction peak at 2θ [38]. With this, the evolution of the FWHM of (111) diffraction peaks is used to study the growth of (111) crystallite size during isothermal annealing. From Figure 5.21, it is observed that the FWHM of (111) decreases only after 200 hours of isothermal annealing. This means that the initial decrease in porosity observed in Figure 5.21 is due to coarsening of the fused Cu NPs with minimum grain growth. Hence, the improvement in shear strength for the first 200 hours was suggested to be due to coarsening because the (111) crystallite size did not increase. Moreover, from the SEM images, it was observed that the size of the agglomerates increases. However, as ageing time increases to 200-800 hours, the volume fraction and size of the (111) crystallites increase. Therefore, grain growth due to surface

diffusion between the fused Cu NPs is the likely mechanism. Though nano-crystalline materials are inherently unstable and room temperature grain growth of nano-crystalline Cu has been reported, grain growth of these nano-sized materials may be hindered by impurities, porosity and a narrow grain size distribution [39]. Therefore, the presence of porosities after bonding could have slowed down grain growth that led to no obvious change in the (111) FWHM during the first 200 hours. As isothermal ageing proceeded beyond 200 hours, the porosity was reduced as shown in Figure 5.19. This is accompanied by the decrease in (111) FWHM which indicates the growth of (111) crystallites that led to an increase in shear strength shown in Figure 5.21. From this observation, it shows that the (111) crystallites have grown after 1000 hours of thermal ageing even though the ageing temperature (i.e. 150°C) is lower than the bonding temperature (i.e. 200°C). It is reported that Lorentzian broadening of XRD peak line profiles is related to the size of the diffracting domains which can be deemed as the size of the crystallite [40]. From Figure 5.21, it is observed that the size of the (111) oriented crystallites increased after 200 hours of isothermal ageing, i.e. decrease in (111) FWHM. Hence, the narrower the FWHM, the bigger the crystallites size. As ageing time proceeded, the size of the crystallites continued to increase up till 800 hours. This is accompanied by the increase in shear strength. After 800 – 1000 hours, growth of (111) crystallites has saturated. Though the growth is minimal, a slight dip in shear strength was observed at 1000 hours. This could be due to oxidation of the Cu NPs that caused a slight dip in shear strength.

Figure 5.21 Graph of shear strength and line width (FWHM) as a function of ageing time

5.5 Conclusion

Cu NPs with a size range of 20 – 100 nm has been demonstrated to provide a feasible alternative for low temperature ($\sim 200^{\circ}\text{C}$) bonding process with good mechanical and electrical properties. Proper optimizations of process parameters can yield good mechanical properties, according to MIL-STD-883E, that can be employed in die attach and interconnect applications. From these studies, the heating rate is crucial to achieve good joint strength as it affects the rate of volatilization which in turn affects the degree of growth and densification of Cu NPs. Rapid volatilization should be avoided as it causes non-uniformed volatilization of organic materials which eventually affects the fusion of Cu NPs. However, if the heating rate is too slow, the fusion of Cu NPs will begin at the lower temperature regime. This leads to an increase in the effective radius of the NPs at the peak temperature which ultimately causes those NPs to lose its ability to fuse at low temperature in the later stage.

In addition, an uncovered structure will enable faster removal of organic materials as compared to a covered structure. Therefore, a suitable heating rate

and soaking duration need to be considered for different types of structures used. To establish a suitable heating rate, *in-situ* electrical resistance measurements can provide a quick and easy way to understand the fusion behavior of the Cu NPs. A measurable shear strength of 4 MPa can be achieved at a low processing temperature of 200°C without any application of pressure. To improve the bonding quality, a pressure of 5 MPa with a soak time of 10 minutes at 200°C can be adopted. From the microstructure studies, it is shown that the densification of the sintered layer is more noticeable with the introduction of bonding pressure. This can be attributed to the increase in the number of contact points and/or areas among Cu NPs and with the bonding interfaces that leads to a stronger solid neck formation among Cu NPs due to closer distance between Cu NPs and material deformation that increases the sintering rate. Strong bonding among Cu NPs will lead to higher bond strength as a higher energy is needed for the crack to propagate across the fused Cu network. Neck size of the fused Cu NPs should be used to estimate joint integrity.

With the optimum processing parameters chosen, a 150°C isothermal ageing test in air up till 1000 hours was carried out to study the reliability of such joints. Microstructures analysis, μ XRD, and shear strength were used to understand the joint reliability. No obvious cracks were observed though the ageing test was carried out in air. After ageing for 1000 hours, it has a preferred (111) texture with an increase in shear strength (~3 times) due to growth of crystallites and reduction in porosity. With these preliminary results, it shows that these Cu NPs can be a viable alternative as a die-attach material that is used for low temperature process applications.

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Chapter 6

Cu NPs as Interface Materials for High Power LEDs

In the previous chapter, the joint stability of die – die bonding using Cu NPs has been demonstrated. In this chapter, the application of Cu NPs as a die-attach material in high power Light Emitting Diode (LED) packaging will be studied and demonstrated. To test its applicability, the process method and parameters used in the experiments follow closely with the industrial settings. These LEDs dice were coated with Cu NPs paste and placed onto a Ag-coated alumina substrate. These Cu NPs pastes were then sintered under N_2 condition in a benchtop reflow oven with a peak temperature of 280°C. The as-bonded properties are compared directly with the conventional AuSn solder, which is commonly used for high power LEDs applications. The results are encouraging as the mechanical, electrical and optical properties are comparable to AuSn solder. To understand the long-term reliability of Cu NPs, reliability tests such as isothermal ageing and thermal cycling tests were carried out on these LEDs modules as well. Mechanical, electrical, optical and microstructure evolution were characterized and correlated with one another to have a better understanding of the Cu NPs performance as a die-attach material. From all these results, it does validate the potential of Cu NPs to replace current high temperature solder materials such as AuSn, though further tuning of process parameters and type of bonding interfaces should be looked into subsequently.

6.1 Introduction

The number of power semiconductors applications has been increasing in the recent times. Hence, the demand for high temperature lead free solder materials is also increasing. These solders provide mechanical strength, electrical and thermal conduction between the die and the substrate. In the LED application, the interface material for die-attach plays a major role in its ability to dissipate heat and to maintain its mechanical and electrical reliability [1]. As LED lighting applications expand, new die attach material is required in LED packaging to satisfy the demanding requirement of higher thermal conductivity to achieve the desired performance and reliability of the devices. Currently, there are a few materials such as gold-tin (Au-Sn), gold-germanium (Au-Ge) and gold-silicon (Au-Si) that are being studied extensively [2]. These solders are used as die-attach for LED emitters to minimize thermal resistance between the LED die and substrate. This allows the LED to drive to higher currents and thus achieving higher light flux density reliably. However, there are some challenges such as the presence of voids from the non-wetting of solders with substrate/die and formation of IMCs within layer that will degrade the LED's mechanical, electrical, thermal and optical properties over time. Moreover, the cost of AuSn solder is high. Therefore, nano-size metallic particles (<50 nm) which possess good mechanical, electrical properties and high thermal conductivity have been studied extensively since it has a high possibility of replacing the current die-attach materials [3-6]. These nano-metallic particles are chosen instead of micron-scale metallic particles because of its ability to be sintered spontaneously at a lower temperature due to higher surface energy. As a result, the pressure needed for bonding can be reduced significantly. Thus, a new die-attach material with the ability to be processed at a lower temperature, has a better or comparable performance than conventional solder and has a lower price is therefore highly sought after.

Thus, the Cu NPs paste that was studied in the previous chapters will be investigated extensively for high power LEDs applications. The purpose of this chapter is to apply the previous understanding of this material to do a feasibility and reliability study of using Cu NPs as a die attach for LEDs applications. The

characterization of the electrical, mechanical and optical performance of the LEDs after subjecting it to thermal aging will be carried out to assess its potential and possible challenges when integrating it to the current manufacturing processes.

6.1.1 Experimental Methods

The SiC-based LED chips from Cree, Inc. ($0.98 \text{ mm} \times 0.98 \text{ mm}$) used in this study are InGaN-based white LED devices that are vertically conducted with Au finish as the back metallization. To demonstrate the usability of Cu NPs, commercial Au80Sn20 solder (NC-SMQ51SC) purchased from Indium Corporation was used as a comparison. After applying the Cu NPs paste to bond the samples, the devices were reflowed under N_2 ambient with the profile of 200-220-260-280°C for a total cycle time of ~ 7 min, with a heating duration of 1.5 min at each temperature in a 5-zone reflow oven (Sikama Falcon 5C).. For AuSn samples, 180-240-280-320°C with a total cycle time of ~ 5 min (as recommended by the supplier), with a heating duration of 1 min at each temperature for AuSn samples. A higher reflow temperature of 320°C is needed for AuSn to ensure that the solder has fully melted during the reflow process. After bonding, mechanical strength was characterized using shear tester (similar to those explained in Chapter 3) and electrical measurements were carried out using a 2 probe method. The resistance across LED die/bonding layer (nano Cu)/Ag metallization on the substrate was obtained from the slope of the I-V curve measured. To examine the optical properties of the two different die attach materials, their luminescence peak wavelength of the LEDs was measured using a spectrometer (Newport OSM 100) with a 3 V voltage applied. Figure 6.1 is a typical sample of the single chip LED after reflow.

To test the long-term thermal reliability of Cu NPs, 1000 hours of isothermal ageing test at 200°C in air and 300 cycles of thermal cycling (-55°C to 125°C) were carried out. Mechanical, electrical and optical properties were then correlated with the microstructure evolutions observed.

Figure 6.1 As-reflow single-chip LED module

6.2 Principle Outcome

6.2.1 Overview of Cu NPs as a LEDs die attach material

From the previous chapter, it is known that factors such as higher peak temperature, a suitable heating rate of 17°C/min or even higher at 40°C/min but with the aid of forming gas, can help to enhance the fusion of Cu NPs. Since the peak sintering temperature is 280°C in this study, it is likely to enhance fusion of the Cu NPs that can result in higher mechanical strength.

To validate the feasibility of using Cu NPs as a replacement for Au-Sn solder as a die attach, the LEDs modules that were bonded using Cu NPs paste were tested and compared with LEDs that were bonded with AuSn solder after bonding. The cross-sectioned SEM image of the as-bonded LED modules with Cu NPs or AuSn solder are shown in Figure 6.2.

Figure 6.2(a) Overview of the LED module bonded with (a) Cu NPs paste with (b) Zoom-in view of the bonded layer; (c) AuSn solder with (d) Zoom-in view of the bonded layer (scale 10 µm)

From Figure 6.2(a) and (b), it is observed that the bonded layer using Cu NPs shows uniformity across the die-attach layer. There is no sign of cracks or big pores, and no IMCs were observed. However, for AuSn solder, different color contrast can be observed in Figure 6.2(d). This possibly indicates the presence of AuSn IMC (darker contrast) and areas that are Au rich (lighter contrast) as reported in literature [7]. This difference in color contrast is commonly observed when using solder alloy as a die-attach material due to different atomic mass of materials. Based on literature, the most commonly found Au₈₀Sn₂₀ IMCs are AuSn, AuSn₂ and AuSn₄ [8,9]. The contrast in the FESEM images observed in this study is similar with those previously reported (shown in Appendix C [9]).

6.3.1.1 Mechanical Measurements

The mechanical integrity of the LED modules was evaluated using die shear strength. The die shear strengths were measured using a Dage 4000 Multi-purpose BondTester using the same parameters as what was described in Chapter 3.

Table 6.1 Shear strength of LED modules bonded with Cu NPs and AuSn solder

Materials	Sintering/reflow temp (°C)	Shear Strength (MPa)
Cu NPs	280	43.54 ± 17.00
Au80Sn20	320	50.52 ± 0.01

From Table 6.1, the shear strength of the LED modules for both die-attach materials after sintering or reflow are comparable. This is not surprising as the bonding layer between LED die – Cu NPs – substrate as observed from the SEM images is dense and without significant voids (Figure 6.2(a) and (b)). As mentioned in Chapter 5, to attain a shear strength of >6 MPa, the amount and degree of necking between Cu NPs should be as high as possible.

Figure 6.3 shows a higher magnification cross-sectioned FESEM image of the Cu NPs on the LED die after shearing. Significant amount of necking between Cu NPs clusters can be observed. This shows that if the heating rate and peak temperature is high, though the processing time is short, good fusion between these Cu NPs can still be attainable.

Figure 6.3 FESEM cross-sectioned image of Cu NPs on the LED die after shear test

Though the shear strength of Cu NPs samples is slightly lower than that of AuSn, the absence of applied pressure and lower processing temperature of Cu NPs during sintering make it compatible and attractive for this application. Besides, as the sintering of Cu NPs is based on solid state atomic diffusion rather than a change of state from solidus to liquidus as in Au-Sn solder reflow, the LED die will not move during the reflow process, thus enabling placement of a higher density of LED dice on the substrate. Still, the question of whether the presence of nanopores within the bonded layer will have negative effects on its electrical properties remains. Hence, electrical measurements were taken to ascertain its electrical properties after sintering.

6.3.1.2 Electrical Measurements

To measure the electrical resistance of the bonded LEDs, a two-probe method was used. The electrical resistance was obtained from the slope of the measured I–V graphs. Resistance was measured across the LED die/ die-attach material (Cu NPs or AuSn)/Ag metallization on the substrate. Table 6.1 shows the maximum reflow or sintering temperature of the 2 materials and their respective

resistance. A schematic diagram of how the measurements were carried out is shown in Figure 6.4.

Figure 6.4 Schematic diagram of the electrical resistance measurement setup of LED module

Table 6.2 Electrical resistance of LED modules bonded with Cu NPs and AuSn solder

Materials	Max Fusing/Reflow Temperature (°C)	Electrical Resistance (Ω)
Cu NPs	280	2.389 ± 0.219
Au80Sn20	320	9.117 ± 5.969

Higher average electrical resistance from the LED modules bonded with AuSn solder was observed. The thickness for both die-attached materials is similar. Hence any thickness effect is not the main reason for the large difference in measured resistance. This means that the higher resistance is likely due to the higher electrical resistivity of AuSn ($16.4 \times 10^{-8} \Omega \cdot \text{m}$ at 20°C) as compared to Cu NPs electrical resistivity that is expected to range between $0.6 \times 10^{-8} \Omega \cdot \text{m}$ – $1.68 \times 10^{-8} \Omega \cdot \text{m}$ at 20°C [10]. The expected range of electrical resistivity for Cu NPs is calculated based on the electrical resistivity of bulk Cu measured at 20°C and normalized with the amount of porosities within the sintered Cu NPs layer. Meanwhile, as observed in Figure 6.2(c) and (d), LED that was bonded with AuSn comprises of IMCs and alloys (represented by the different color contrast). These phases created some interfaces within the bonded layer that could possibly increase the overall electrical resistance. On the other hand, though Cu NPs

bonded layer was porous, the pore sizes were all in nano-size range. In addition, there were no IMCs within the die-attach layer. Hence it does not affect the electrical properties significantly.

6.3.1.3 Optical Measurements

The optical properties of LEDs bonded with the two different types of die-attach materials, Cu NPs and AuSn solder, were also measured and compared to ensure its optical capabilities. The light intensity of the LED modules was measured using a spectrometer with a 3 V voltage supplied to the LED stack. The illumination peaks appeared at 450 nm and 600 nm, which correspond to white LED. In addition, the intensity from these two die-attach materials showed a slightly higher light intensity from the Cu NPs LEDs as compared to AuSn LED samples (Figure 6.5). This might be due to the formation of micro-cracks in the intermetallic layers of the AuSn solder (Figure 6.2(d)), which affected the thermal resistance and caused a lower intensity [1]. In addition, the higher intensity could also be due to the Cu NPs having a lower electrical resistance as compared to AuSn since the same amount of voltage was applied.

Figure 6.5 Photoluminescence spectra of Cu NPs and AuSn die-attach LEDs operated at 3 V at room temperature

6.3.1.4 Thermal Resistance Comparison

From the optical intensity comparison, it is observed that when the LEDs were bonded with Cu NPs, it shows a higher intensity. Such an occurrence could be due to lower thermal resistance of Cu NPs as well. To do a relative comparison of the thermal resistance between Cu NPs and AuSn solder, a transient thermal analysis was carried out using T3ster® located at Nanyang Polytechnic School of Engineering [11]. For this experiment, a constant current of 100 mA was initially applied to the LED module until thermal equilibrium of 45°C was reached. Subsequently, the current was lowered to 1 mA so that it would not heat up the samples, yet sufficient for measurements of the change in temperature across the LED modules. The temperature of the LED modules was measured up till 1000 s and was used to compare the temperature dissipation response for both die-attach materials. In the measured temperature curves shown in Figure 6.6, the y-axis represents the change in junction temperature measured and the sensing current used was 1 mA. As observed in Figure 6.6, at the same given time, the decrease in junction temperature for Cu NPs samples is lower than the LEDs that were bonded with AuSn solder. This means that the Cu NPs is able to conduct heat better as compared to those LEDs that were bonded with AuSn solder. Such better thermal conductivity in Cu NPs could be due to the absence of intermetallics compounds that create multiple interfaces across bonding layer found in those LEDs samples bonded with AuSn solder. Thus, with better thermal conduction, it will have less Joule heating effect of the device which will also contribute to a lower electrical resistance as shown in Section 6.2.1.2. The lower electrical resistance and higher thermal conductivity of LED samples that were bonded with these Cu NPs will in turn have a higher light intensity i.e. brighter as observed in Section 6.2.1.

Figure 6.6 Measured temperature with time for Cu NPs and AuSn LED samples

With these mechanical, electrical, optical and thermal measurements, it further demonstrates the feasibility of using Cu NPs paste as a die-attach material for high power LED modules. The next step is to understand the reliability of the Cu NPs bonded LEDs.

6.3.2 Reliability Tests

In this section of reliability tests, the focus will be on joints that are formed with sintered Cu NPs. Hence the reliability of AuSn solder will not be included in this section. From the initial measurement data shown in Section 6.3.1, it has demonstrated the feasibility of using Cu NPs as a die-attach material for LEDs applications. However, nano-sized porosities were observed within the sintered Cu layer and at the bonding interfaces. To evaluate the long-term high temperature storage stability of sintered Cu NPs joint, the mechanical, electrical and optical properties were studied in detail after isothermal ageing test for a specific duration. Though similar tests have been carried out in Chapter 5, the isothermal ageing test in this section will be carried out on actual LED modules (without encapsulation) and at a higher temperature of 200°C. This temperature was chosen based on JEDEC Standard testing for general high temperature

storage life test (JEDEC Standard No. 22-A103E). This means that the Cu NPs are sandwiched between two different interface materials and subjected to higher thermal stress. Besides long term thermal stability examination, thermomechanical reliability test was carried out through thermal cycling as well. The joint strength (shear strength) and microstructural changes of the samples after each reliability test will be evaluated.

6.3.2.1 Isothermal Ageing

Isothermal ageing test under air condition was carried out at 200°C for 1000 hours. At every 250 hours, 5 LEDs samples were taken out from the oven for shear strength, electrical, optical and microstructure evaluation. The shear strengths obtained were plotted as a function of ageing time as shown in Figure 6.77.

Figure 6.7 Shear Strength of Cu NPs LED die after 1000 hrs of thermal aging

From the initial shear strength (ageing time 0 hr), it is observed that the shear strength of the LED modules was ~42 MPa. However, as ageing time proceeded to 250 hr, a ~30% drop in shear strength was observed. After 1000 hr of ageing,

the shear strength decreased to 9 MPa. From the previous chapter, it was shown that as ageing time increases, the overall shear strength increases. However, in this study, the opposite trend was observed. This could be due to two reasons. First, the maximum temperature for Cu NPs sintering was done at 280°C, and hence the initial shear strength was in fact much higher than the previous data found in Chapter 5 (~ 4 MPa). This means that the Cu NPs were well-fused at time zero and further isothermal annealing would lead to more grain growth, since it was aged at 200°C instead of 150°C as studied in Chapter 5. From Figure 6.8, the microstructure evolutions of the sintered Cu NPs are shown. From the images, no obvious big cracks or voids were observed after 1000 hours of ageing. Only further densification and growth, especially towards the bottom substrate, have been observed in Figure 6.9, where pores are smaller and the degree of necking among Cu NPs is high. However, from the fracture surfaces of the samples after annealing for 250 hrs, cracks with width ~5 μm were seen. At the end of 1000 hrs, the crack width grew to 9 μm (Figure 6.10). This increase in the size of the cracks may be due to the continual fusion of the Cu NPs after sintering. As these fused Cu NPs continued to grow, it could further densify. This would lead to some shrinkage and may cause cracks at the bond interface and among the fused Cu NPs to form. Such discontinuity could not be caused by the IMCs between Cu and Au as they are completely mixable based on the Cu-Au phase diagram as attached in Appendix B. The failure at the Cu/Au interface may be due to capping layers of the Cu NPs at the interface being more difficult to volatilize because of the more closed structure.

Hence, when there are cracks among fused Cu NPs, the cracks can grow and propagate easily and lead to lower shear strength. From the surface fracture analysis using FESEM images, the crack propagation path is derived. Figure 6.11 shows the schematics diagram of crack propagation across the 2 bonding interfaces and within the sintered Cu NPs layer.

Figure 6.8 Microstructural changes of Cu NPs bonded onto LED

Figure 6.9 Microstructures of Cu NPs (a) just after sintering, (b) after 1000 hours at 200°C

Figure 6.10 Fracture surfaces of LED dice and substrate after (a) 250 hours (30 μm scale) (b) 1000 hours of isothermal ageing at 200°C (100 μm scale)

Figure 6.11 Schematic diagram of crack propagation through Cu NP layer

In terms of electrical measurements, 5 samples were measured before ageing and the same 5 samples were measured again at every 250 hours of isothermal ageing. In Figure 6.12, the electrical resistance at the start of ageing was about 2.5 Ω .

However, as ageing proceeded to 250 hrs, the electrical resistance increased to $\sim 4 \Omega$ and remained relatively constant till 1000 hrs. From these electrical data results, it does appear that the electrical and mechanical properties do not share any direct co-relationship as there was no significant change in electrical resistance after 250 hrs of ageing. This is because though there were still nano-pores and/or cracks present within the bonded layer and at the bonding interfaces, electrons can still flow through the layer since majority of the Cu NPs had fused with one another to provide conduction paths for electrons to flow. This is shown in the FESEM images (Figure 6.8) of the sintered Cu NPs that even after 1000 hrs, no big voids or cracks that could cause poor joint strength was observed.

However, when the light intensity of a same LED module was measured at every 250 hrs of isothermal ageing, it is observed that the peak intensity at 450 nm (corresponding to blue light) and a 2nd broad peak which corresponds to the emission of the phosphor coating are lower and broadening of peaks are observed. The lower light output after every 250 hrs may indicate the increase in electrical resistance at a same given voltage. This increase in electrical resistance could be due to presence of copper oxide, as the LED was not encapsulated and the ageing was done under air condition. This could result in oxidation of copper that leads to a lower light intensity as copper oxide has a higher electrical resistance than copper. In addition, the increase in the amount of small voids at the bonding interfaces that were observed in Figure 6.7 could also contribute to the increase in junction temperature that lead to lower light output. The photoluminescence spectra of the same LED module at every 250 hrs of isothermal ageing are shown in Figure 6.13.

Figure 6.12 Electrical resistance of Cu NPs with Au LED from 0 – 1000 hrs of isothermal ageing test

Figure 6.13 Photoluminescence spectra of Cu NPs on Au metallization of a white light LED (blue + phosphor) operated at 3 V at room temperature for different ageing period

6.3.2.2 Thermomechanical Reliability

The performance of Cu NPs bonded on LED modules after thermal cycling was also studied. The purpose of thermal cycling test is to accelerate the effects of thermal expansion mismatch between different materials across the die and substrate. Therefore, in this study, 15 LEDs samples were subjected to a temperature cycling profile of -55°C to 125°C with 1 hr/cycle for 300 cycles. At every 100 cycles, 5 samples were taken for mechanical and microstructure analysis.

From the thermal cycling test results, a small decrease in shear strength was observed after 100 cycles and a drastic decrease in shear strength was observed after 200 cycles (Figure 6.14).

Figure 6.14 Shear strengths of Cu NPs bonded LEDs after thermal cycling

This initial small decrease in shear strength is possibly due to horizontal cracks between the Cu NPs and Au metallization of the LED substrate (6.15(a)).

Subsequently after 200 thermal cycles, there are two distinct fracture paths: the presence of vertical cracks within the Cu NPs layer and more distinct horizontal cracks along the Ag and Cu NPs bonding interfaces (6.15(b)). These two occurrences could potentially give rise to a significant drop in shear strength. This is even more obvious for samples that have undergone 300 cycles where delamination between Ag and Cu was severe and the vertical cracks across the Cu NPs layer had grown bigger. As a result, the shear strength dropped to ~ 3 MPa after 300 cycles.

The delamination from the bonding interfaces as observed from the FESEM images (Figure 6.15 (b) and (c)) could be due to the different types of materials present throughout the entire LED module. The LED module consists of a silicon carbide (SiC)-based InGaN LED die with Au metallization, and Ag-plated metallization on a ceramic (Al_2O_3) substrate.

Figure 6.15 FESEM images of Cu NPs LED modules after (a) 100 cycles, (b) 200 cycles, (c) 300 cycles (Scale: 20 μm)

Hence, there will be a large CTE mismatch across the entire LED module that can potentially cause thermal mismatch stresses during temperature cycling. Table 6.3 shows the CTE of the materials mentioned above.

Table 6.3 CTE of materials across the entire LED module [12]

Material	Coefficient of Thermal Expansion at 20°C (10^{-6} K^{-1})
Au	14
Ag	18
Cu	17
SiC	2.77
Al ₂ O ₃	4.5

It has been reported that the thermo-mechanical properties of sintered Ag particles are good due to the presence of pores that lower its elastic modulus. With a lower elastic modulus, it will transfer less of the thermally induced stresses from the CTE mismatch between the LED chip and substrate [13].

However, the presence of pores and grain growth in the sintered Cu NPs may reduce the shear strength due to creep dislocations piling up at the grain boundaries and form microcavities [14]. This is because the thermal stresses at these pores, micrograins and interfaces between fused Cu NPs clusters could be sufficiently high to produce dislocation creep during thermal cycling due to stress-concentration effect [2] [14]. In addition, most studies [13-15] that have reported good thermo-mechanical properties of sintered NPs joints were based on Ag NPs bonded on Ag coated ceramic substrates. Hence, the CTE mismatch was lower, and strong and stable bonds at the bonding interfaces could be achieved as they were bonded between the same material. In the current study, the chip and substrate metallization were Au and Ag, respectively, and the die-attach layer was Cu NPs. Moreover, the total contact area at the bonding interfaces is <100% (Figure 6.16) since these Cu NPs do not melt and wet the bonding surfaces like conventional solders materials. Hence, there are nanopores at the bonding interfaces as well. This could possibly become an additional area for thermal stress accumulation that allows cracks to propagate and weaken the shear strength after cycling.

As for the vertical cracks within the sintered Cu NPs, they could be formed due to the occurrence of thermal stresses during the cycling process. Before the start of cycling, it is observed from Figure 6.4 and Figure 6.11(a) that not all Cu NPs were well fused. Those points where there was no or little necking between Cu

NPs could become potential areas for cracks to form during the thermal cycling test. From the fracture surfaces of the as-bonded samples (Figure 6.17), it is observed that there were small “islands” on the fracture surfaces. This further proved that due to weak bonding among sintered Cu NPs clusters at certain regions, they allowed cracks to move through easily. Such voids or cracking could be due to fast solvent volatilization during sintering [16]. Though these voids were not big initially, they could act as stress concentration points that led to bigger voids and separation between the fused Cu NPs when subjected to thermal cycling. Hence, this type of failure is classified as Type 1 failure, which was explained in Chapter 5.

Figure 6.16 Voids were present at the bonding interface between Cu NPs and (a) Ag, and (b) Au metallization after sintering

Figure 6.17 (a) FESEM image of sheared surface of an as-bonded LED chip (b) Zoomed-in on the “islands” of sintered Cu NPs clusters

6.4 Conclusion

In this chapter, the feasibility of using Cu NPs as a die-attach material for high power LEDs application is demonstrated. In the first part of the study, AuSn solder, which is the current material used in such application, was used to provide a reference for the Cu NPs. From the electrical, thermal and optical characterizations, it is observed that the Cu NPs has a lower electrical resistance than AuSn solder, which resulted in a higher light intensity when a same voltage was applied. With a higher thermal conductivity, the Cu NPs LED also has a lower junction temperature as compared to AuSn one. This was achieved even though the peak temperature for processing Cu NPs was only 280°C, which is 40°C lower than AuSn peak reflow process. The shear strength for both materials was comparable as well.

Some reliability tests such as long-term high temperature storage and thermal cycling were carried out on the Cu NPs samples. From the long term high temperature storage test, a reduction in shear strength after 1000 hrs at 200°C was obtained though no big voids or cracks were observed, and the LEDs dice were still intact. Such observation could be due to the further non-uniform densification of Cu NPs during isothermal ageing. Moreover, the contact area between the bonding interfaces (Au and Ag) and Cu NPs layer was not

continuous as the Cu NPs do not melt and wet the surfaces like conventional solders. Hence, adhesion failures were observed during shear test after prolonged aging.

Furthermore, due to the dissimilar bonding interfaces, it leads to thermal stress accumulation during thermal cycling. Hence delamination at the bonding interface was also observed after 300 cycles. In addition, due to the fast volatilization of solvent, the fusion between Cu NPs were not very strong. Therefore, vertical cracks across the sintered Cu NPs layers were observed after 300 cycles. With all these cracks and delamination at the interfaces, it weakened the overall shear strength. Therefore, though Cu NPs shows potential and feasibility to be used as a replacement for AuSn solder for high temperature solders, the processing parameters and materials used at bonding interfaces have to be optimized and designed to achieve good and reliable joints.

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Chapter 7

Discussion and Future Work

This chapter concludes the overall work presented in the previous chapters. Firstly, a general discussion starting from the sintering mechanism of different metallic NPs used by researchers and the challenges that needs to be addressed and overcome were mentioned. More importantly is that at the current moment, Ag NPs and Au NPs are being mentioned more often than Cu NPs due to their high resistance to oxidation and ease to handle. Another area that were lacked of further research is the long-term reliability studies of Cu NPs. Thus further in-depth studies need to be carried out and discussions from each chapter of this thesis will be given in the following sections of this chapter. In addition, some reconnaissance work that were done but not mentioned in the main chapters of this thesis is briefly included in this chapter. After which key conclusions from this work will be identified and some outstanding questions such as the bondability of Cu NPs to other common metallic surfaces such and other mechanical properties such as hardness and tensile strength can be further study to understand the mechanical properties difference between Cu NPs and bulk copper. All these are listed as some of the recommendations for future work.

7.1 General Discussion

In this study, the sintering mechanism of metallic Cu NPs is being studied extensively. Though many studies on metallic NPs have been carried out by various research groups, the type of metallic NPs, synthesis technique and size of NPs were largely different. This poses a huge challenge for direct comparison between studies. Moreover, these studies were more focused and developed for Ag NPs, which is much easier to handle as they do not oxidize easily and can be processed under air condition. However, Ag is much costlier than Cu and it suffers from ion migration. Therefore, Cu is the next alternative because it has already been used throughout the electronics industry as a trace, interconnect and pad material. This minimizes compatibility issues. Moreover, when compared to Ag and Au, it is cheap and abundant. In addition, the thermal and electrical conductivity of Cu is relatively high, which makes it suitable for use in interconnects and die-attach applications. Though studies on Cu NPs have started, the long-term reliability data of Cu NPs is still lacking, partly due to the fact that the development of the basic understanding of Cu NPs is still in progress.

Hence in this thesis, it is divided into 3 main parts. The first part looks into the development of a novel and fast technique to understand the sintering mechanism and behavior of these Cu NPs when subjected to different sintering parameters by measuring the electrical resistance during sintering. This is important for the next 2 chapters of the thesis as the Cu NPs paste will be used for bonding applications and its long-term reliability will be studied. Discussions on the various chapters will be explained in the following sections with some outstanding questions to be raised.

7.1.1 Understanding Cu NPs Sintering Mechanism Through *In-Situ* Electrical Resistance Measurement

The primary objective of this work is to characterize the Cu NPs and evaluate its feasibility as a low temperature bonding material. In Chapter 4, the sintering mechanism and behavior of Cu NPs using a simple technique of *in-situ* electrical resistance measurement during sintering was investigated. The change in electrical resistance measured during sintering is used to correlate with the

results obtained from thermal analysis techniques such as TGA and DSC that were carried out separately. Since these Cu NPs are capped with organic layers to prevent agglomeration, aggregation and unwanted fusion prior to thermal treatment, they are not electrically conductive. However, as it undergoes thermal treatment, these capping layers are removed from the Cu NPs surfaces and fusion of these particles occurs, thus forming electrically conductive paths. By studying the change in electrical resistance during sintering, the onset temperature of evaporation of the organic materials and fusion of Cu NPs can be known for different sintering conditions. A simple model was developed to determine the dominant sintering mechanism at the initial stage based on the resistance change with time during isothermal annealing. In addition, it is observed that the rate of change of resistance during heating up is related to the rate of removal of organic materials at different sintering conditions. Therefore, this technique is useful for designing optimal sintering conditions for all types of organic passivated metallic NPs. In addition, it can also provide a quick check on whether these NPs are fully sintered each time. In addition, with the observation in the change in electrical resistance during sintering, the ability to capture the immediate microstructure at each time step for subsequent analysis is made possible. This means that freezing the microstructure of the Cu NPs at certain stages based on the change in electrical resistance can be done and it is useful for microstructure evolution study for deeper understanding of the dominant sintering mechanism. For the Cu NPs studied, the dominant sintering mechanism when heating rate is low ($7^{\circ}\text{C}/\text{min}$) is identified as surface diffusion. This related well with the FESEM images as large amount of porosities were still present after sintering. For the heating rate of $17^{\circ}\text{C}/\text{min}$ samples, the proposed model with the parameters extracted suggests that the dominant sintering mechanism is due to lattice diffusion from the surface. Lattice diffusion is commonly reported to cause densification since the source of material originates from the grain boundary. However, in this study, the proposed model suggests it was lattice diffusion from the surface and no densification was observed. This could mean that the source of material during diffusion is from the nanoparticle surface, hence no densification was observed. Thus, in this thesis, it is still classified as surface diffusion. However, the model and technique are limited to the initial stage of sintering, as minimum or no shrinkage of sintered Cu NPs layer is

assumed in the model and the electrical resistance does not change too much after the initial stage of sintering. Hence, an advanced model that considers resistivity instead will be useful since the thickness of the sintered Cu layer will have a great influence on the electrical performance.

7.1.2 Enabling Low Temperature Bonding Using Cu NPs

After establishing a fast and simple technique to characterize the Cu NPs at different sintering conditions, it shows the potential of such Cu NPs to be sintered at a low temperature (i.e. 200°C). In Chapter 5, based on the basic understanding of the sintering behavior of Cu NPs, different sintering conditions were studied for bonding. The focus here is on low temperature bonding applications and its long-term thermal stability.

In the first part of Chapter 5, a suitable heating rate was re-established since it is now a sandwich bonding structure which is different from Chapter 4. The effects of bonding temperature, pressure and type of bonding environment were studied. A change in the mechanistic bond formation was observed when bonding was done at 300°C. It is observed from the studies that when bonding was done at low temperature (200°C), the shear strength does not increase much after prolong annealing. However, when bonding temperature increases to 250°C and 300°C, longer hold time at peak temperature will cause the shear strength to increase substantially.

As the goal is to develop good fusion of Cu NPs at low temperature, applying a pressure during bonding is being investigated to improve the joint integrity. Bonding pressures between 1 – 5 MPa were exerted during the bonding process. It is noticed that the dominant sintering mechanism is still based on diffusion process up till 3 MPa. Ductile failure was observed on the fracture surfaces for samples that were bonded with a 5 MPa pressure. Hence by introducing pressure, it does improve the bond strength. Though the introduction of pressure can lead to a better joint integrity at low temperature, pressureless bonding is preferred in some applications.

Since we know that the fusion of such Cu NPs is dependent on the removal of passivation layers, a method to increase the rate of passivating layers' removal should be looked into. Based on the results found in Chapter 4, the removal of the passivating layers is very fast and possible when high heating rate is used under formic acid vapor environment as compared to N₂ environment. Hence formic acid is only introduced at peak temperature to allow volatilization and fusion to occur only at the maximum temperature. Results show a less porous microstructure with strong necking between Cu NPs and good bond integrity though high heating up rate (40°C/min) and shorter total cycle time were used. Therefore, from this study, it is established that it is possible to sinter these Cu NPs at a low temperature of 200°C and below

The most important factor in determining the bond property is the effectiveness of passivating layer removal. Such removal will enable more uniform necking among Cu NPs clusters that results in higher shear strength. It is also observed from the different microstructures of various sintering conditions that porosity of the sintered layer cannot be taken solely to estimate the joint integrity. The degree of necking formed by those fused Cu NPs has a more direct effect on the overall joint integrity.

Lastly, long-term thermal stability of sintered Cu NPs joints was studied. From the results, the shear strength of the joints increases with time and porosity decreases when isothermally annealed at 150°C for 1000 hours in air condition. Grain growth of these Cu NPs after isothermal annealing was observed using ex-situ μ XRD. These preliminary reliability results provide a new insight towards the stability of such sintered Cu joint that allows it to be tailored for different high power die-attach applications.

7.1.3 Cu NPs Bonding Application in High Power LEDs Die Attach

After studying the effects of sintering parameters on its microstructure and shear strength, the final objective of the thesis is to adopt this material for usage as a die-attach material for high power LEDs applications since the sintered Cu NPs joints show good long-term stability in Chapter 5. When the LEDs dies were bonded with Cu NPs or AuSn solder, the LEDs bonded with Cu NPs demonstrated comparable or even better mechanical, electrical and optical

performance as the die-attach material. It is worth pointing out that the peak sintering temperature of Cu NPs was only 280°C, which is 40°C lower than the peak reflow temperature of AuSn solder. Though the mechanical strength of the joints is slightly lower for Cu NPs due to the presence of small voids at the bonding interfaces, the Cu NPs joints outperform AuSn ones in terms of electrical and optical properties. This is likely due to the presence of IMCs in the AuSn joints that would increase the interface resistance and thus affect the overall electrical performance. On the other hand, for Cu NPs joint, the electrical resistance is lower due to the good electrical properties of Cu. Moreover, the thermal conductivity for the Cu NP layer is higher than that of the AuSn one. Though pores were present in the sintered Cu joint, the optical performance of the Cu NPs joint is still better than that of AuSn. This could be due to the LEDs that were bonded with Cu NPs having a lower electrical resistance as compared to AuSn joint. In addition, it could be due to the Cu NPs having a higher thermal conductivity than AuSn solder.

With these preliminary data, reliability tests such as high temperature isothermal storage and thermo-mechanical reliability tests on the LEDs that were bonded with Cu NPs were carried out. From the isothermal ageing test, the shear strength of the Cu NPs joint decreases with time. This decrease in shear strength could be due to the weak interface bonding between Au/Cu NPs and Ag/Cu NPs. As pointed out earlier, the joining of Cu NPs to the bonding surfaces does not involve melting of the Cu NPs paste. Hence the contact area between Cu NPs and bonding surfaces is less than 100% after bonding. With the presence of small voids at the bonding interfaces, these voids might coalesce and form micro-voids as ageing time increases. This allows cracks to propagate easily along the interfaces. The other possible reason for failure to occur at the interface is the densification of Cu NPs during ageing. From the FESEM images, it is observed that the amount of porosities across the sintered layer changes and the Cu NPs located near the bonding interfaces have further densified. This would cause more voids at the interfaces to form that allow cracks to propagate easily. Therefore, as ageing time increases, an increase in mixture of adhesive and cohesive fracture surface was observed. Lastly, oxidation, is a possibility in this reliability study as all these LEDs samples were not encapsulated, and signs of

oxidation were observed in the Cu NPs at the edges of the die. However, in actual fully encapsulated devices, this may not be a key factor.

For the thermo-mechanical reliability tests of the sintered Cu NPs joints, due to the large CTE mismatch between Cu NPs, die and substrate, and the presence of voids along bonding interfaces, cracks were observed along the bonding interfaces and within the sintered layer. Though there have been reports stating that a porous sintered layer has a lower elastic modulus that will transfer less of the thermally induced stresses from the CTE mismatch between die and substrate, the contact between sintered Cu NPs and bonding surfaces before thermal cycling must be good. To improve the contact between Cu NPs and bonding interfaces, a higher peak sintering temperature of $>280^{\circ}\text{C}$ is required for good sintering process between Cu NPs and substrate, and fusion among Cu NPs. In addition, other ways of improving the contact at bonding interfaces is important as the sintering of Cu NPs does not involve a change of solidus to liquidus state that wets the bonding surfaces.

7.2 Reconnaissance work not included in main chapters

When formic acid was introduced during the bonding process, one interesting observation that is not included in the main chapters is the change in color of the Cu NPs during bonding under different bonding environment. To correlate the change in electrical resistance with color of the Cu NPs paste, snapshots of the Cu NPs at different sintering time and ambient are shown in Figure 7.1.

Figure 7.1 Color change during bonding under (a) N2 (b) Formic Acid

It is observed that no significant color change was observed when bonding was done under N_2 after fast heating up to 200°C . However, under formic acid environment, color change was observed only at peak bonding temperature. This shows the effective removal of passivating layers and the onset of fusion with significant degree of necking between Cu NPs. Since surface plasmon resonance absorption of metallic Cu nanoparticles results in a red color, the reddening observed in Figure 7.1 for formic acid assisted sintering at 10 minutes implied the production of metallic Cu nanoparticles [5]. Hence the change in electrical resistance can be simply detected by changes in color of the Cu NPs and the latter can provide a quick way of gauging the final microstructure and bond strength of the sintered Cu layer at different bonding parameters.

7.3 Outstanding Questions

Through the work that was described in this thesis, we have shown the feasibility of Cu NPs to be used as a die-attach or for 3D interconnections. However, further studies have to be done on improving the contact area between Cu NPs and bonding interfaces. As sintering of metallic NPs, unlike conventional solder, does not involve melting, hence the wetting of bonding interfaces needs to study further. As shown in the results presented in Chapter 6, the degree of wetting of the bonding interfaces have a significant impact on the joint reliability. Though the mechanical strength and electrical properties of the bonds are good, after long-term high temperature storage or thermal cycling tests, these small voids along the bonding interfaces do have a negative impact on the joint integrity. Hence an in-depth focus on the bonding interfaces with Cu NPs would be worth studying. In addition, in most part of this work, the bonding of Cu NPs paste was done on Cu surfaces. Other metallic surfaces such as Au, Ag, Sn, Ti can be looked into since they are the common materials found in electronics devices. It might be interesting to look into the bonding of Sn surfaces with Cu NPs. As Sn melts at 232°C , it can flow into the pores and cracks of sintered Cu to form IMCs and affect the mechanical, electrical and reliability of the joint. The final microstructure might be a composite structure with fiber-like IMCs that could strengthen the overall mechanical properties of the sintered joint as they can act as crack deflection or stopping barrier. The rate of IMCs formation would also

be an interesting area to study since the reaction of Cu and Sn has been studied widely but not the reaction of Cu NPs with Sn.

In Chapter 4, the sintering and densification of Cu NPs is studied through a home-made test structure to provide a quick understanding of the sintering process. Based on this simple technique, the sintering mechanism was derived by studying the change in electrical resistance with temperature and time. In addition, it also provides a quick and simple method of qualifying the material in terms of the Cu NPs size and formulation. However, cracking of the Cu NPs paste has caused some challenges in measuring the electrical resistance during sintering. Therefore, further improvement can be made to the test structure to allow similar amount and thickness of Cu NPs across every test samples.

In Chapter 5, we have shown the effect of sintering parameters on the final microstructures of Cu NPs and proposed a sintering model. Therefore, future work can include some modelling to further investigate the sintering mechanism of Cu NPs under different ambient since they lead to different microstructures. More work can be done to examine the relationship between contact area at bonding interfaces with Cu NPs as they have a huge impact on the mechanical shear strength and reliability of the joint. The relationship between porosity and the mechanical properties of the sintered Cu NPs can be studied and compared with bulk copper. This includes the hardness and elastic modulus. As mention previously, change in resistivity with time for different sintering condition can be used to develop another sintering model that can predict the densification stage of Cu NPs sintering.

After studying the mechanical and electrical properties of Cu NPs, in Chapter 6, we have demonstrated the possibility of adopting these Cu NPs paste on actual LED modules. It does demonstrate good potential as compared to commercial AuSn solder. However, since the mechanism involved does not include melting like conventional solders, more study on increasing the contact area at bonding interfaces is needed. This may include changing the degree of roughness of the bonding surfaces, and ways to reduce the CTE mismatch such that they can be used as a die-attach material for low CTE die materials such as SiC and GaN. Cracking across sintered joint is observed, especially after ageing or thermal

cycling test. This will affect the electrical, mechanical and thermal properties. Hence further modification, enhancement and study of the formulation of Cu NPs paste such as adding suitable number of nanowires into the Cu NPs can possibly help to minimize cracks, strengthen and improve the joint reliability [6].

Last but not least, besides all the suggested areas that can be further explored based on the current studies, there are other related research works that are being pursued by others in the author's research group. This includes using the Cu NPs paste to bond tiny chips on flexible substrates as well as making Cu NPs ink for printing interconnects on flexible organic substrates.

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Appendix A

Based on MIL-STD-883E method 2019.5 Die shear strength Failure criteria, a device which fails any of the following criteria shall constitute a failure.

- Fails die strength requirements (1.0X) of Figure 1.
- Separation with less than 1.25 times the minimum strength (1.0X) specified in Figure 1 and evidence of less than 50 percent adhesion of the die attach medium.
- Separation with less than 2.0 times the minimum strength (1.0X) specified in Figure 1 and evidence of less than 10 percent of adhesion of the die attach medium

Figure 1 Die shear strength criteria (minimum force versus die attach area)

The die area used in this study is 1 mm^2 , which is equivalent to $15 \times 10^{-4} \text{ IN}^2$.

Based on the graph in Figure 1, the minimum force will be 0.6 kg.

Thus, Shear strength = $0.6 \times 10^6 = 0.6 \text{ MPa}$ (1X), 0.75 MPa (1.25X), 1.2 MPa (2X)

Figure 2 Failure interface of (a) Bottom Chip (b) Top Chip

All the sintered Cu NPs joints have a shear strength ≥ 2 MPa and the sintered joints show cohesive failure with $>50\%$ coverage. Thus, they have passed the MIL-STD-883E method 2019.5 failure criteria.

Appendix B

Cu-Au phase Diagram

Figure 3: Cu-Au phase Diagram

Image taken from: http://www.factsage.cn/fact/documentation/binary/binary_figs.htm

Appendix C

Figure 4: Different phases of AuSn IMCs

Image taken from: Lee, Teck Kheng, Sam Zhang, C. C. Wong, A. C. Tan, and Davin Hadikusuma.

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