STUDY OF COPPER-ALUMINIUM HIGH TEMPERATURE DIE-ATTACH MATERIAL WITH DIFFERENT ALUMINIUM WEIGHT PERCENTAGE

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ABSTRACT

High temperature die attach material has excellent corrosion resistance, good ductility, good electrical volume resistivity. Therefore, die attach materials have been introduced for electronic packaging. Nanoparticles have high surface energies and was developed for the use at high operational temperature. There are a lot of type of materials have been developed to prepare nanopaste which is very costly. Besides, electrical characteristic also been another issue. Through this study, Cu and Al nanoparticles were introduced in order to synthesize nanopaste by varying the aluminium percentage at 20%, 40%, 60% and 80%. CuO compound was found in the nanopaste indicated the presence of oxidation process. The use of organic additives was controlled during sintering process. The nanopaste were sintered at 380°C in order to study electrical, physical properties through scanning electron microscope and X-ray diffraction thermal characteristic. The dwell time was set at 30 minutes while for the ramp rate was set at 5°C/min respectively. AlCu, $AlCu_3$, and Al_3Cu_2 were found in Cu-Al nanopaste through XRD peaks. The solid state diffusion exhibited strong absorption peak in XRD diffractogram. The melting point of copper and aluminium nanoparticles showed 196±1°C and 224±1°C respectively. The Cu_{20}-Al_{80} nanopaste sample showed the lowest melting point compared to others. The electrical properties increased gradually with the increasing of aluminium weight percent content. Cu_{20}-Al_{80} die attach nanopaste showed 1×10^4 $(\text{ohm-cm})^{-1}$ with the highest electrical conductivity value obtained. Formation of bigger grains and structures were viewed in the nanopaste samples in which aluminium content increased from 20% to 80%. Incomplete coalescence of particles were observed due to the aggregation of nanopaste which occurred during the nanopaste sintering process. The nanopaste sample showed promising electrical conductivity results for high aluminium content sample and therefore, aluminium proved to be a good metal.

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ABSTRAK

Suhu tinggi mati bahan melekat mempunyai rintangan kakisan yang sangat baik, kemuluran yang baik, daya tampung kelantangan elektrik yang baik. Oleh itu, bahan melampirkan mati telah diperkenalkan untuk pembungkusan elektronik. Nanopartikel mempunyai tenaga permukaan yang tinggi dan dibangunkan untuk digunakan pada suhu operasi yang tinggi. Walau bagaimanapun, banyak jenis bahan telah dibangunkan untuk menyediakan nanopaste yang sangat mahal. Selain itu, ciri-ciri elektrik juga menjadi isu lain. Melalui kajian ini, Cu dan Al nanopartikel diperkenalkan untuk sintesis nanopaste dengan mengubah peratus aluminium pada 20%, 40%, 60% dan 80%. Kompaun CuO yang terdapat di nanopaste menunjukkan kehadiran proses pengoksidaan. Penggunaan bahan tambahan organik dikawal semasa proses sintering. Nanopaste disinter pada suhu 380 °C untuk mengkaji sifat-sifat fizikal elektrik melalui pemeriksaan mikroskop elektron dan ciri haba difraksi sinar-X. Waktu kediaman ditetapkan pada 30 minit manakala untuk kadar ramp ditetapkan pada 5 °C / min masing-masing. AlCu, AlCu3, dan Al3Cu2 ditemui di Cu-Al nanopaste melalui puncak X ray difraktogram. Penyebaran keadaan pepejal menunjukkan puncak penyerapan yang kuat di difraktogram X ray difraktogram. Titik lebur tembaga dan aluminium nanopartikel menunjukkan 196 ± 1 ° C dan 224 ± 1 °C masing-masing. Sampel nanopaste Cu20-Al80 menunjukkan titik pencairan terendah berbanding dengan yang lain. Sifat elektrik meningkat secara beransur-ansur dengan peningkatan kandungan peratus berat aluminium. Cu20-Al80 mati melekat nanopaste menunjukkan 1 × 104 (ohm-cm) -1 dengan nilai kekonduksian elektrik tertinggi yang diperolehi. Pembentukan bijirin dan struktur yang lebih besar dilihat dalam sampel nanopaste di mana kandungan aluminium meningkat daripada 20% kepada 80%. Coalescence zarah tidak lengkap diperhatikan kerana pengagregatan nanopaste yang berlaku semasa proses sintering nanopaste. Sampel nanopaste menunjukkan hasil

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kekonduksian elektrik yang menjanjikan untuk sampel kandungan aluminium yang tinggi dan oleh itu, aluminium terbukti menjadi logam yang baik.

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TABLE OF CONTENTS

Abstract iv

Abstrak v

Aknowledgements vii

Table of Contents viii

List of Figures x

List of Tables xi

List of Symbols and Abbreviations xii

CHAPTER 1: INTRODUCTION 1

1.1 Background and Problem Statement 1

1.2 Research Objectives 4

1.3 Outline for Research Report 5

CHAPTER 2: LITERATURE REVIEW 6

2.1 Increasing Demands in High Temperature Electronic Packaging 6

2.2 Die Attach Material 6

2.3 Nanoscale Die Attach Pastes 15

2.4 Organic Additives 16

2.5 Cu Nanopaste 18

CHAPTER 3: MATERIALS AND METHODOLOGY 19

3.1 Introduction 19

3.2 Cu-Al Nanopaste Formulation Materials 22

3.2.1 Cu-Al Nanopaste Formulation 22

University of Malaya

3.2.2 Cu-Al Nanopaste Sintering **25**

3.3 Investigation of Physical, Electrical, and Thermal Characteristics for Cu-Al 26

3.3.1 Physical Characterization 27

3.3.1.1 Scanning Electron Microscope (SEM) 27

3.3.1.2 X-Ray Diffraction (XRD) 28

CHAPTER 4: RESULTS AND DISCUSSION 32

4.1 XRD Analysis 32

4.2 DSC Analysis 37

4.3 Electrical Conductivity Measurements 41

4.4 SEM Microstructures Analysis of Cu-Al Nanopaste having Different Al Weight Percentage Content 44

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS 48

5.1 Conclusions 48

5.2 Recommendations 50

REFERENCES 51

University of Malaya

LIST OF FIGURES

Figure 1: Melting temperature of various electronic material systems and optimum functional temperature range. 11

Figure 3.1: Flow chart for methodology of research project. 20

Figure 3.2: Characterization technique of Cu - Al nanopaste. 21

Figure 3.3: Process flow for Cu-Al die attach nanopaste formulation. 24

Figure 3.4: Experiment setup for sintering Cu-Al nanopaste in air glas flow. 26

Figure 4.6: Organic nanoparticles layer burn off sequence during sintering. 34

Figure 4.7: X-Ray Diffraction diagram for the pure Cu and Al nanoparticles as well as sintered Cu and Al nanopaste (87% weight percent nanoparticles content) with different Al weight percentage. 36

Figure 4.8: DSC plot for Cu-Al nanopaste having various nanopaste weight percent content sintered at 380°C. 39

Figure 4.9: Error bar plot of electrical conductivity for Cu-Al nanopaste (87% weight percent content) with increasing Al weight percentage. 43

Figure 4.10: SEM image at 10,000× magnification of Cu_{80}-Al_{20} nanopaste (a), Cu_{60}-Al_{40} nanopaste (b), Cu_{40}-Al_{60} nanopaste (c), Cu_{20}-Al_{60} nanopaste (d) 46

University of Malaya

LIST OF TABLES

Table 1: Thermal conductivity and electrical properties for various elements. 3

Table 2: Thermal conductivity and performance index for various die-attach systems. 10

Table 3.1: Raw materials that applied for Copper-Aluminium nanopaste formulation. 22

Table 3.2: Cu-Al die attach nanopaste formulation. 23

Table 3.3: Samples for Cu-Al nanopaste for Al weight percentage variation content by having fixed nanoparticles content with total of organic additives weight percent content at 87.0%. 26

Table 4.1: Enthalpy of melting and melting point for Cu-Al nanopaste samples having different aluminium weight percent content. 40

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LIST OF SYMBOLS AND ABBREVIATIONS

Cu	:	Copper
Al	:	Aluminium
CuO	:	Copper oxide
AlCu	:	Aluminium Copper
Au	:	Gold
Ge	:	Germanium
SiC	:	Silicon Carbide
CTE	:	Coefficient of Thermal Expansion
SiC	:	Silicon Carbide
In	:	Indium
XRD	:	X Ray Diffraction
DSC	:	Differential Scanning Calorimetry
SEM	:	Scanning Electron Microscope
Hz	:	Hertz
MPa	:	Megapascal
I-V	:	Current Voltage
K	:	Thermal Conductivity
GaN	:	Gallium Nitride

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CHAPTER 1: INTRODUCTION

1.1 Background and Problem Statement

Integrity part of electronic package formation from power device technology especially high temperature die attach or interconnect technology is crucial in this era of globalization world since it provides an electrical, thermal and mechanical interface between the substrate and device (Kisiel & Szczepański, 2009). Power device of die attach material should provide excellent electrical property and thermal conductivity as well as how the change in temperature affect size of the object for example between the substrate and die, ability to provide optimum coating between substrate and die, high fatigue resistance and also high wettability property (Manikam & Cheong, 2011; Chin *et al*., 2010).

The most concern issue in the field of die attach which made from the condition at high temperature are the liquidity as well as solidus temperature. Besides that, thermal and electrical conductivity characteristics seriously affected the condition as well. The reliability of the material itself hold tightly for the interfaces of bonding between die attach material together with the substrate (Lalena *et al*., 2002; Hartnett & Buerki, 2009). Die attach material acts as interface between the substrate and die especially in high temperature electronic packaging. Besides, die attach forms a fundamental in a well-defined process as well.

There are a lot of die attach materials with high temperature which developed in this era of globalization, for example gold (Au) solder alloys, germanium (Ge)-doped metal alloy, high temperature laminating resin epoxy, lead based solder metal alloys, zinc (Zn) solder metal amalgamate, and silver with micron scale sized metal pastes. This is normally the particle size measurement. All type of die attach materials are categorized

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from the low to moderate range of peak operating temperature which is in between 200 and 400 °C (Manikam & Cheong, 2011). However, Au thick films and Au thermo-compression technology which is more than 400°C and this temperature fall into the high temperature operating category and this showed the exceptional case among all the high temperature die attach materials (Manikam & Cheong, 2011; Meyyappan *et al*., 2003), Au–Si (Manikam & Cheong, 2011 & Naidich *et al*., 1998), Au–nickel (Manikam & Cheong, 2011; Suganuma et al., 2009), Au–Ge (Manikam & Cheong, 2011; Hagler et al., 2011; Chidambaram *et al.,* 2010) and Au–indium (In) based solder alloys (Manikam & Cheong; Lee *et al*., 1993; Shi *et al.,* 2000). Pure gold and silver solution were utilized with excellent technology in which force and heat is applied simultaneously and also the formation of resistive layer. Certain processes done in order to ensure the successful of the coating application. However, silver and gold are at high range cost of solutions in terms of manufacturing considerations.

There is the rise of interest in die attach material which produced from the high presence of heat energy in different fields with the development and introduction of nanoscale material in this new era of globalization world. During sintering process, the translation to lower processing temperature is resulted from the minimization of size at the nanoparticle scale level which resulted in larger surface area with high energy for such material. Besides that, the purpose to perform the process is to lower down the melting points versus the material that conducted in large quantity itself (Groza & Zavaliangos, 2003; Groza, 1999). Nanoscale form of pastes can be used for sintering process in order to synthesize die attach and there is reflow needed. Meanwhile this is not similar to solder alloys in which nanopaste scale could be sintered for die attach. There is no concerns as well regarding floating and die shifting exists and therefore solidus state mechanism process is not needed during sintering process (Lu *et al.,* 2004; Zhang & Lu, 2002; Bai *et al.,* 2006; & Bai *et al*., 2007). This resulted in issues solving which is related to joint-

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reliability concerns and also inter-metallic compound formation (Zhang & Lu, 2002; Lu *et al.,* 2007; Lu *et al.,* 2004).

Another positive point for nanoscale die attach materials is its much lower Young's modulus when there is a comparison for bulk density of materials for the die attach systems (Wakuda *et al.,* 2007 & Wakuda *et al*., 2008). This could be accredited to the formation of permeable pores within the material (Manikam & Cheong, 2011; Chin *et al*., 2010; Zhang & Lu, 2002; Lu *et al.,* 2007). On top of that, huge development is needed in order to drive the high temperature electronics (Chin *et al*., 2010). However, excellent voltage performance, mass production in manufacturing and reliability is to be considered as well. Nanoscale die attach pastes have been proven to have exceptional thermal conductivity attributes, and are suitable for high temperature applications. The most developed wide band gap of semiconductor is the silicon carbide technology.

Table 1 differentiate the thermal resistivity and electrical conductivities of the various metal and element which have been ranked from the highest to the lowest in terms of electrical conductivities and thermal resistivity characteristics of elements that showed in periodic table.

Table 1: Thermal conductivity and electrical properties for various elements (Callister & Rethwisch, 2007).

Properties	Silver	Copper	Gold	Aluminium
Electrical property (9105 (ohm-cm)$^{-1}$)	6.24	5.96	4.50	3.77
Thermal conductivity (W/m-K)	427	402	317	238

Copper nanoparticles have been combined together with aluminium nanoparticles in an organic nanopaste formulation based on the idea where the bonding process took place. Cu and Al both have the second and fourth best electrical conductivity in which they have

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the ability to conduct and also Cu and Al have good thermal conductivity. Besides that, Cu and Al are relatively at lower price compared than both gold and silver (Cao *et al.*, 2011; Callister & Rethwisch, 2007; Kearns, 2004). Thus far, there has not been a concept presented for die attach applications at high temperatures using these metallic elements at the nanoscale level.

1.2 Research Objectives

The objective of this research work is to synthesize high temperature die attach material using copper and aluminium nanoparticles to produce nanopaste through sintering process and thus to characterize the characteristics of the nanopaste. Such high temperature die attach material undergo characterization through electrical, thermal, as well as physical properties, and therefore below listed with objectives:

1. To synthesize Copper-Aluminium die attach nanopaste system using metallic nanoparticles.
2. To sinter Cu-Al nanopaste by varying aluminium weight percentage.
3. To characterize Cu-Al nanopaste for physical, thermal and electrical investigation.

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1.3 Outline for Research Report

This research report basically divided into five chapters. Chapter 1 is an introduction of overview for high temperature die attach material which involving challenges encountered especially silicon carbide power devices, research objectives as well as the outline for this research. Chapter 2 presents the literature review cum with the latest findings and together with problems encountered. Besides that, chapter three discussing for the materials and methodology and also materials needed in this research work. The equipments used also discussed in the systematic methodology. While for chapter four discussed the findings and results from this research work. The final chapter discussed is conclusion as well as recommendations are laid out.

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CHAPTER 2: LITERATURE REVIEW

2.1 Increasing Demands in High Temperature Electronic Packaging

High temperature electronic packaging has come to the fore in research due to the ever increasing demands for more robust devices in such industries as deep drilling, aircraft, automotive and space exploration (Manikam & Cheong, 2011; Chin *et al.,* 2010; Werner & Fahrner, 2001). The workhorse semiconductor technology, silicon (Si) is limited in terms of its operation junction temperature which is below 200 ^{o}C and voltage blocking capabilities (Johnson *et al.,* 2001). Wide band gap semiconductors which included gallium nitride (GaN) as well as silicon carbide (SiC) on the other hand provide solutions to such issues (Chin *et al.,* 2010; Johnson *et al.,* 2001). Wide band gap semiconductors have higher breakdown fields and thermal conductivity capabilities and can therefore operate in harsh environments or at high temperatures (Friedrichs *et al.,* 2000). The materials used in high temperature electronic packaging must be able to withstand such conditions. Thus, the challenge from the issue is to develop and formulate the new packaging and interconnection material which can withstand at high temperature.

2.2 Die Attach Material

Plastic housing material is a type of material which consist the ability to perform in hot temperature. The most crucial development in such area need emphasizing in high power SiC electronic packaging which included interconnects or die attach, case, encapsulation, passive heat exchanger and processor chip (Coppola *et al.,* 2007). Interconnect technology, the silicone gels, or plastic housing for alternative power equipment technology is very important in which it has the ability to form a fundamental part of the electronic package.

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Besides that, such joining material also has the ability to provide a tensile property, thermal conductivity and electrical interface between the substrate and the equipment (Kisiel & Szczepański, 2009).

Optimization in the electrical property and thermal conductivity, good adhesion for the die and substrate, and small coefficient of thermal expansion (CTE) between die and substrate material are significantly crucial in order to obtain excellent surface contact point and acceptable loads applied from the weakening of materials for repeated cycle loading (Chin *et al.,* 2010).

There is various of high temperature die attach materials have been studied, for example lead based type of solder alloys (Manikam & Cheong, 2011; Suganuma, 2003; Plumbridge *et al*., 2007; Abtew & Selvaduray, 2000), gold metal alloys (Kisiel & Szczepański, 2009), optimum temperature resin-epoxy (Kisiel & Szczepański, 2009; Krishnamurthy *et al*., 1992), zinc (Zn) solder alloys (Islam *et al*., 2005; Cheong, 2011; Lee *et al*., 2007; & Wang *et al*., 2010), germanium solder metal alloys (Manikam & Cheong, 2011; Lalena *et al*., 2002) and micron-silver (Ag) pastes (Manikam & Cheong, 2011; Zhang & Lu, 2002). However, such type of solder alloy normally fell from low to middle operating range which is between 300 and 400 ^{o}C (Manikam & Cheong, 2011). Gold wafer-bonding and diffusion bonding technology and the formation of thick films to produce electronic devices and surface mount devices are examples although there are still some inconsistency which fall into the high temperature functioning category which is more than 500 ^{o}C (Manikam & Cheong, 2011, Meyyappan *et al*., 2003), Au–Si (Manikam & Cheong, 2011; Meyyappan *et al*., 2003, Naidich *et al*., 1998), Au nickel (Manikam & Cheong, 2011; Suganuma *et al*., 2009), Au–Ge (Manikam & Cheong, 2011; Hagler *et al*., 2011; Chidambaram *et al*., 2010) and Au–indium (In) based solder alloys (Manikam & Cheong, 2011; Lee *et al*., 1993; Shi *et al*., 2000). The common die attach

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materials involving lead-tin in which it is particularly large size die for high temperature applications. The advantages of using such type of materials involved high ductility as well as optimal thermal conductivity range. The low melting points enable the eutectic composition to occur at 183 °C. Performance, reasonable cost, and processability offered by solders. Such alloy was acknowledged as mature products. The use of leaded die attach materials on large dies resulted in low stress concentration points on the dies due to the characteristics of leaded solder alloy and its edge due to its excellent ductility. Till date, there is the absence of lead free die attach materials that work efficiently for huge power and big die. There is very limited number of alloying systems and this resulted in current plan that small power device dies with developed solutions for die attach to be qualified (Suganuma *et al.*, 2009). However, from manufacturing point of view, gold metal is a high-priced metal in producing electronic mount surfaces. The function or property of the electronic surface material should possess melting point which is higher than 600 ºC in order to make it suitable for high temperature applications (Manikam & Cheong, 2011). Furthermore, high thermal conductivity is extremely crucial in order to evaporate the bulk flow kinetic energy and internal energy that derived from the die to the substrate and therefore the electronic material must also acquire high thermal contact, as well as, possess low fractional change in length per unit change in temperature at constant pressure in order to minimize the formation of pressure that caused by the change in temperature (Manikam & Cheong, 2011).

To relate both power generated heat as well as heat deflection temperature, performance index is therefore being used in order to change the selection of an electronic packaging material. Heat flow among the material according to Fourier's Law for steady state one directional, *x*, was showed as below (Ashby *et al*., 2004):

$$q = \frac{K}{x}\Delta T \tag{2.1}$$

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where K is the thermal conductivity while q is the total heat input per unit area and ΔT is the change of temperature. The difference in temperature is affected by the buildup strain, ε, in the die attach material (Ashby *et al*., 2004):

$$\varepsilon = \alpha \Delta T \tag{2.2}$$

where α is the CTE. Equation (2.3) is thereby derived by combining Equation (2.1) and (2.2) (Ashby *et al*., 2004):

$$q = \frac{\varepsilon}{x}\left(\frac{K}{\alpha}\right) \tag{2.3}$$

Thus, a bond joint material with high value of K/α, which is defined as performance index, M could be further minimized in a given heat flow from the die, the buildup strain (ε) in which equation as per below (Ashby *et al*., 2004):

$$M = \frac{K}{\alpha} \tag{2.4}$$

The larger value of performance index indicated the bonding joint material has larger capacity for productivity in coordinating heat thermal energy from the die to the substrate, making less heat energy being absorbed and to be stored in the atoms of bonding material. Less thermal energy being stored will eventually cause less vertical displacement of the existing force among the atomic distance, which resulting less damage of the electronic packaging. In line with globalization trend and direction, the performance indices for various electronic packaging materials are being quantified for future differentiation (Table 2).

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Table 2: Thermal conductivity and performance index for various die-attach systems.

Die-attach system	**Thermal conductivity, K (W/m K) at 25 °C**	**CTE, *α* (×10^{-6}/K)**	**M = K/ *α* (×10^{6} W/m)**	**Ref.**
Metal Paste				
(i) Silver nanopaste	201-242	19-20	10.0-12.6	Mei *et al*., 2012
(ii)Silver-Copper nanopaste	159	13	12.2	Tan *et al.,* 2015
(iii) Ag-Al nanopaste	124	8	15.4	Manikam *et al*., 2012
(iv) Ag hybrid paste	136-251	19.7*	6.9-12.7	Suganuma *et al*., 2012; Kahler *et al*., 2012
(v) Cu micropaste	94	16.5*	5.7	Kahler *et al*., 2002
(vi) Ag micropaste	80-222	19.7*	4.1-11.2	Zhang & Lu, 2002; Lu *et al*., 2004
Metal film				
(i) Au	-	—	—	Del Castillo *et al.,* 2006
(ii) Au-In	-	—	—	Mustain *et al.,* 2010
(iii) Ag-In	-	—	—	Chuang & Lee, 2002
Conductive glass	60-80	16-25	2.4-5.0	Kisiel & Szczepański, 2009
Solder alloy				
(i) Zinc	77-115	20-32	3.7-4.0	Kim *et al*., 2009; Gancarz *et al.,* 2012
(ii) Au	27-59	12-16	2.3-3.7	Kisiel & Szczepański, 2009; Navarro *et al*., 2012
(iii)Lead				
(a) Lead-free	20-67	15-42	1.3-1.8	Abtew & Selvaduray, 2000; Suganuma *et al.,* 2009; Calame *et al*., 2005 Navarro *et al*., 2012; Mei *et al*., 2012
(b) Pb-bearing	23-53	19-30	1.2-1.8	Abtew & Selvaduray, 2000; Suganuma *et al.,* 2009; Calame *et al*., 2005; Shimizu *et al*., 1999; Mei *et al*., 2012
(iv) Bi	7-11	—	—	Lalena *et al*., 2002; Tschudin *et al.,* 2002
Conductive adhesive	1-25	26-53	0.1-0.5	Guan *et al*., 2010

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Symbol "─" means no reported value. Symbol "*" is theoretical value.

In general, electronic interconnection materials can be divided into five categories, which are conductive and excellent in coating, metal alloy, fiber glass, metal coating, and metal paste (Figure 1).

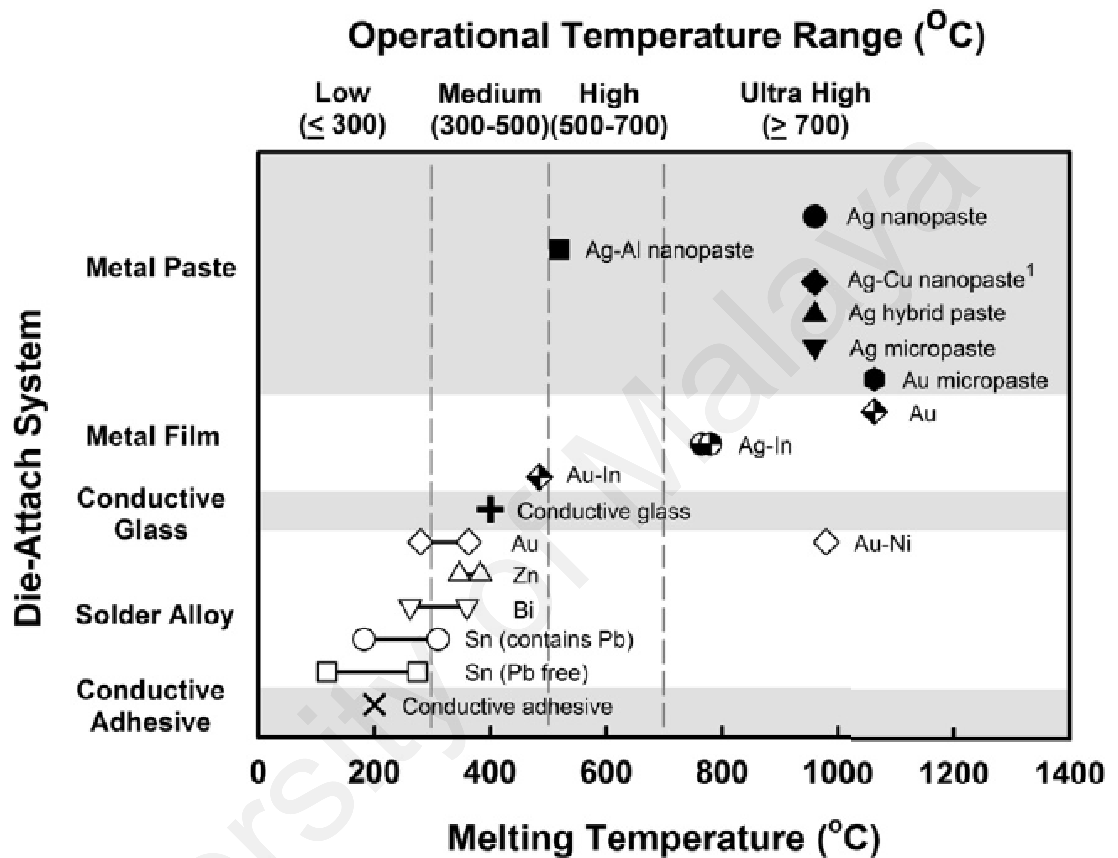

Figure 1: Melting temperature of various electronic material systems and optimum functional temperature range (Tan *et al.,* 2015).

Nowadays, conductive adhesive (Guan *et al.*, 2010; Li *et al.*, 2006; Mir & Kumar, 2008) and titanum based metal amalgamate (load-bearing and free of lead content) (Abtew & Selvaduray, 2000; Suganuma *et al.*, 2009; Turbini, 2007; Calame *et al.*, 2005) are most commonly used in this world for the mentioned electronic packaging materials for level two interconnection, namely between the bond joining material, but these type of materials are having moderate figure such as (0.1-1.7 $\times$ 10^6 W/m) and low melting points as well as boiling point (<260°C), which allow them only acceptable to be applied

for low-temperature range (≤200 ºC) of applications (Figure 1) (Kisiel, R., & Szczepański, 2009). Conductive glass (Kisiel & Szczepański, 2009), gold (Au) (Suganuma *et al*., 2009; Kisiel & Szczepański, 2009; Navarro *et al*., 2012; Weng *et al*., 2013), bismuth (Bi) (Lalena *et al*., 2002; Tschudin *et al*., 2002; Song *et al.,* 2007), and zinc (Zn) (Kim *et al*., 2009; Shimizu *et al*., 1999; Gancarz *et al*., 2012) based metal alloys were frequently introduced. With most of these type of materials showed low range value of results M (2.3-3.9 × 10^6 W/m) from Table 1, this is a disadvantage which limit the application at medium-temperature range from 300°C-500°C (Kisiel & Szczepański, 2009). Although gold and nickel (Ni) are exclusively exceptional bonding joint metal that could be functioned at high-temperature range (≥ 600 ºC) but its high joining fusible temperature at 950 ºC has reached a pitch fall in which the temperature fell suddenly with huge force applied (Kirschman, 1999). The whole system in this globalization world is still able in which they has the capability in operating the temperature from medium to high temperature and this is absolutely crucial in reducing the processing temperature which help in cost saving. The cross section of thermometry line is not able to be modelled because the phase shift variation across lines become significantly important. The major problems with this approach is that it is very difficult to ensure the difference between the rises of the carrier and the die is huge when compared to the rise in the carrier for the most precise of measurements for the change in temperature. Besides that, the next introduction for electronic packaging will be metal coating film as well as metal paste system be it in nanoscale or common scale system. Gold to gold (Del Castillo *et al*., 2006), Au-indium (In) (Mustain *et al.,* 2010), and silver (Ag)-In (Chuang & Lee, 2002) are specific systems with particular design that established a concrete joint through strong solid state and liquid state bonding of metal surface films at a range of temperature from 200 to 450 ºC and pressure of 0.26-41 MPa. The joints formed by gold-gold together with Gold-Indium films could be functioned optimizely at super heat treatment temperature

range (≥ 700 °C), whereas the joint formed by gold to indium film is only limited at moderate temperature range from 310 to 500°C that showed in figure 1. Thermal resistance was measured between 10 and 1000 Hz at the interfaces of the silicon dies and also the carrier as this measurement uses periodic electric heating. Gold bridges are specifically used into the oxide layer by using photolithography which yielded structure as showed in wide bridge. A small bridge and die surface heated a huge periodic current that consist in the wide bridge which carried low current as well as not significant Joule heating. In order to extract the spatially die carrier of thermal resistance which are used together with the analysis provided, the lock-in amplifier provided the amplitude and phase of the fluctuations in temperature. These boundary conditions which is very challenging in reproduction will strongly affect the rises in temperature measured in steady state experiment. There is still a lot of research needed to be studied in which the data clearly showed that the use of resistance values based on the information provided. Quantitative thermal property information of direct relevant for infinite-element modeling is provided from the thermal resistance measurement and the inaccuracy of the data is superb low. This is due to the comparisons of predictions in which the data over a wide frequency range and also the barrier of the heated region to several hundreds of micrometers in order to form the chip carrier. The current technology demonstrated the dimensions of incompleteness for the attachment imperfections which yielded important temperature variations at the die surface and it can be used for guidelines providing. They are especially well suited for in order to measure for the evolution of the die attach material for thermal resistance property when the attachment is needed to repeat heat or moisture stress. This is a target for the ongoing research in which it aims at the volume expansion for the die attach material. The thermal resistance measurement technology explained and described the relationship studied of interfacial flow dimensions as well as local thermal resistances especially if thin die samples could be used. However, this

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diffusion and mixing process technique in order to achieve homogeneous mixture requires additional heating process duration around 27 until 100 hours in order to increase its attach property toughness (Mustain *et al.,* 2010; Chuang & Lee, 2002). Au (Del Castillo *et al.,* 2006), Ag (Zhang & Lu, 2002) and copper (Cu) (Kahler *et al*., 2002) micropastes are alternative source of solutions. These micropastes with property mixtures included metal particles with nanoscale and concrete organic compound joint formation under high temperature at 700°C is produced from sintering technique whilst application of external pressure which is 45 MPa to the sintering process may significantly aid in reducing down the temperature to 250 ºC (Del Castillo *et al.,* 2006; Zhang & Lu, 2002; Kahler *et al.*, 2002). The joint formed by heating process of phase transformation for metal micropaste technique, with or without pressure supplication, has been proven suitable for super high heat treatment temperature range (≥ 700 ºC) of applications with melting point higher than 960 ºC as shown in figure 1 (Del Castillo *et al.,* 2006; Zhang & Lu, 2002; Kahler *et al.*, 2002). Anyhow the supplication of outer surface pressure during sintering process inclined in further complicating the synthesize cum manufacturing process. Silver hybrid nanopaste with small scale (Suganuma *et al*., 2012; Kahler *et al*., 2012) for example a combination of micronano and nanosized metal and elements. Besides that, it included also organic compounds which is silver nanopaste (Lu *et al*., 2004; Bai *et al.,* 2005; Bai *et al.,* 2006; Lu *et al*., 2009; Mei *et al*., 2012) and Cu nanopaste (Krishnan *et al.,* 2012) which is a mixture of metal nanoparticles with as well as organic compound were then developed to further upgrade the sintering at 270-380 ºC without the supplication of exterior factor such as pressure in facilitating the heating process without involving liquefaction process.

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2.3 Nanoscale Die Attach Pastes

Nanoscale die attach pastes have been proven to have exceptional thermal conductivity attributes, and are satisfactory for elevated temperature applications. This has been proven through numerous literature works on Ag nanopaste and nano-composite systems (Pashayi *et al*., 2012; Wakuda *et al.,* 2008; Bai *et al*., 2007; Bai *et al.*, 2006; Lu *et al*., 2007; & Wakuda *et al*., 2007). Nanoscale amalgamation and bonding has been undergo several exploration and examination previously among various metal and elements, however, chemical oxidation and reduction method only qualified for the synthesis process (Manikam *et al.,* 2011; Link & El-Sayed, 1999; Chen *et al*., 2007; Jiang *et al.,* 2005; Dutta *et al.,* 2007; Gonsalves *et al*., 2000). Semiconductor electronic materials can operate at maximum temperature which is 800°C and this a specific feature for semiconductor devices. The final curing temperature was needed to be optimized as the second parameter. In order to reduce the preserve effects on the adhesion characteristics of silicon carbide machine a low curing temperature was desired with respect for sintering of curing temperature. The optimum of the last curing temperature was determined with the property of super microstructure, surface characteristic of the thick film and die attach process which cured at different temperature. High priced metal and element such as gold for thick film of metallization used in previous electronic hybrid packaging. High temperature electronic packaging is needed in core technologies which has ability to transport electric charge especially in electronic joint bonding technology. It was essentially needed to reduce the total amount of biologically and chemical free vehicle which evaporated during joining processing. Two steps process were implemented in this attaching process while a thick film layer was then attached to the cured thick film pattern with large amount of biodegradable material. At various temperature, surface composition and micro-structure of the thick film was cured. The current technology which is exclusively important with the increasing of stability feature is normally carried

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out in room temperature. Low resistance joining material were discussed and it was found that, the upper limit of the electrical conductivity resistance of die-attach material which was estimated was incredibly stable as well as low attach resistance. The amplitude of temperature and phase determination are affected by thermal properties of the silicon die. Nanoparticles metal alloy for the supplication of electronic packaging materials is synthesized at high temperature and this allow new features and properties to appear in research findings. Anyway, no similar method reported in application of the solid particles bonding with different element of nano-sized. The electronic packaging material required these type of raw material which can performed well at high temperature. The supplication of few types of metal elements in forming the paste with different kind of substrate is no longer contemporary due to the application of these type of material also apply in firing and brazing process. However, the synthesis process heating temperatures are in the range of super high which is between 810 and 860 °C (Liu *et al.*, 2001; Zhu *et al.*, 1994; AdlaBnig *et al.,* 1997).

2.4 Organic Additives

The existing and designing of the paste system in organic additives requires extra concentration as it was demonstrated that it could damage the solid state bonding among particles during sintering process (Liu *et al.*, 2010). Therefore, high concentration of organic additives resulted in defective mechanical property which is affected by the strength of the material (Wakuda *et al.*, 2007; Zhigal'skii *et al.,* 2003; Bai *et al.*, 2007; Bowen & Carry, 2002). Nanoparticles with strong atomic surface energy bonding which enable them to undergo the unite of particles to grow into mass at much lower processing temperatures as compared to the materials that bought in lots (Wang *et al.*, 2007; Hu *et al.*, 2010; Bai *et al.*, 2006; Lu *et al.*, 2007; Wakuda *et al.,* 2010; Wakuda *et al.,* 2008; Maekawa *et al.*, 2010; Knoerr *et al.,* 2010). Little amount of pressure up to 3 MPa is still

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supplied for certain cases but at the same time, the crucial and significant factor such as pressure is needed to be removed (Knoerr & Schletz, 2010; Schwarzbauer & Kuhnert, 1989). Nanometre-sized powder can be presented through sintering process in order to achieve the homogeneous state of temperature. By controlling the amount of the use of organic additives such as surfactants and dispersants, the nanoparticles undergo solid bonding reaction without liquefaction state during attaching process. Silicon based compositions is a well-known standard with super high temperature supplication due to the presence of maximum functional temperature range. A wide safety margin is especially needed in order to ensure the high functional temperature of the material. The mechanical properties of the joining material will decrease when there is near the closing of melting point. A complete redesign process is required in order to cope with high temperature environments while for silicon gels only can sustain limited temperature. Diamond has electrical breakdown field and also widest bandgap. Limitations are specifically for packaging material especially for powder cores and ferrites could be molded with specific geometries. In order to obtain high quality substrates, gallium nitride need to be thicken in order to hold high electric fields and gallium is a rare material and therefore this is difficult to ensure the obtaining of the development of gallium nitride. Knoerr *et al.* (2010) stated the properties were explored in order to create the devices for excellent power and high efficiency applications. The maturity of the process and the available infrastructure are the main advantages. The wafers are in high priced and useful for optimum voltage machine. Circuits degradations are specifically related to the non-semiconductor modifications for most of the high temperature studies and the main purpose is to prove the long term reliability. Several teams now focusing on the achievements of reliable and efficient compact system. Converters should be put in the position as close as possible to the actuator in which some converters will be subjected to the tough environment. The lowered density as compared to a material that bought in lot

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helps to generate a much lower mechanical property which is crucial for stress relieve during the failure in increasing volume as temperature increased between the die and substrate.

2.5 Cu Nanopaste

Due to the difficulties supplication of copper in electronic material in joint bonding process, such as the requirement to heat at vacuum atmosphere before the adhesion process, and the heating of transformation process from solid to gas must be carried out in either H_2/N_2 or empty space atmosphere condition (Krishnan *et al*., 2012). In order to reduce the rate of oxidation process, additional four hours is required in cooling down process to remove internal stresses in which the condition requires the presence of N_2 for the process of transformation of powdered copper (Krishnan *et al*., 2012). As a result, an alternative material which is possible to use at high-temperature range, namely silver-aluminium (Manikam *et al.,* 2012) and copper-silver (Tan & Cheong, 2014; Tan & Cheong, 2013) nanopastes, were developed and established to exceed the antedate limitations of Cu nanopastes. These materials not only prioritize in terms of cost in this globalization world in which it is cheaper compared to Ag nanopaste, yet it could also be sintered in air atmosphere without the application of external pressure and additional heating process with short period in transformation, hence making the bonding process becomes simple and convenient. By comparison between silver-aluminium and copper-silver nanopastes, silver-copper nanopaste that was studied previously (Tan & Cheong, 2013; Tan & Cheong, 2014) has provided an optimization point for excellent connection bonding strength, electrical conductivity, as well as the ability to resist damage and corrosion than silver-aluminium nanopaste. This makes silver-copper nanopaste a prospective candidate for high as well as super ultra-high temperature applications.

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CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Introduction

The overall research methodology and characterization techniques were used to study the objectives. Detailed explanation on the materials will first be explained and then followed by experimental procedures and characterization techniques. The Cu-Al die attach material nanopaste is formulated by using suitable surfactants and binders for example organic additives. The sintering profile was chosen based on the optimization parameters stated by Vemal *et.al*., 2012. The aluminium weight percentage content in fusion process is varied while for organic additives weight percentage content is fixed. The combination for organic additives with the best thermal, physical and electrical properties were then analyzed and further characterized with SEM, XRD, DSC and IV test as well.

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Objective 1

To synthesize Copper-Aluminium die attach nanopaste system using metallic nanoparticles.

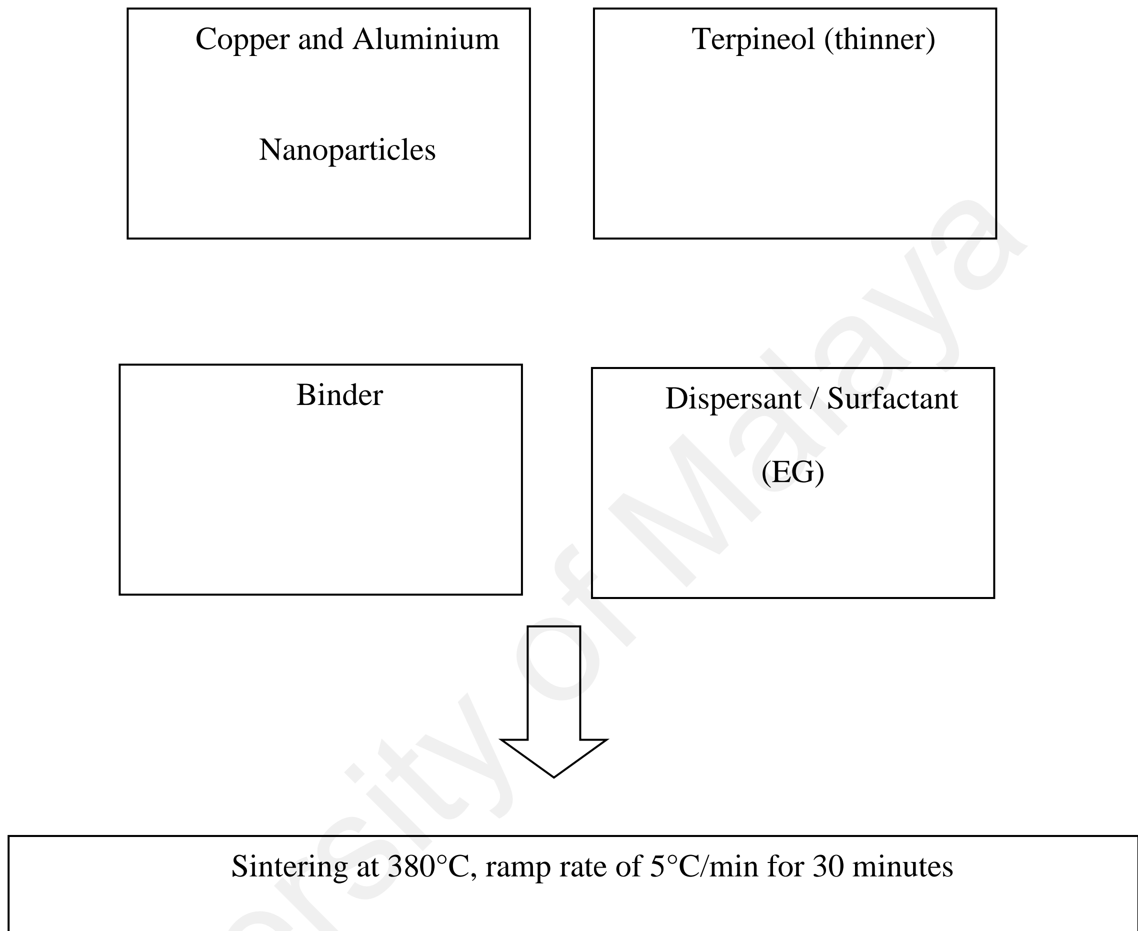

Figure 3.1: Flow chart for methodology of research project.

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Objective 2

To sinter Cu-Al nanopaste by varying aluminium weight percentage.

Objective 3

Characterization of Cu-Al nanopaste for physical, thermal and electrical investigation. The characterization techniques used in this research project were characterized and divided into physical, electrical and thermal analysis in order to study the die attach material.

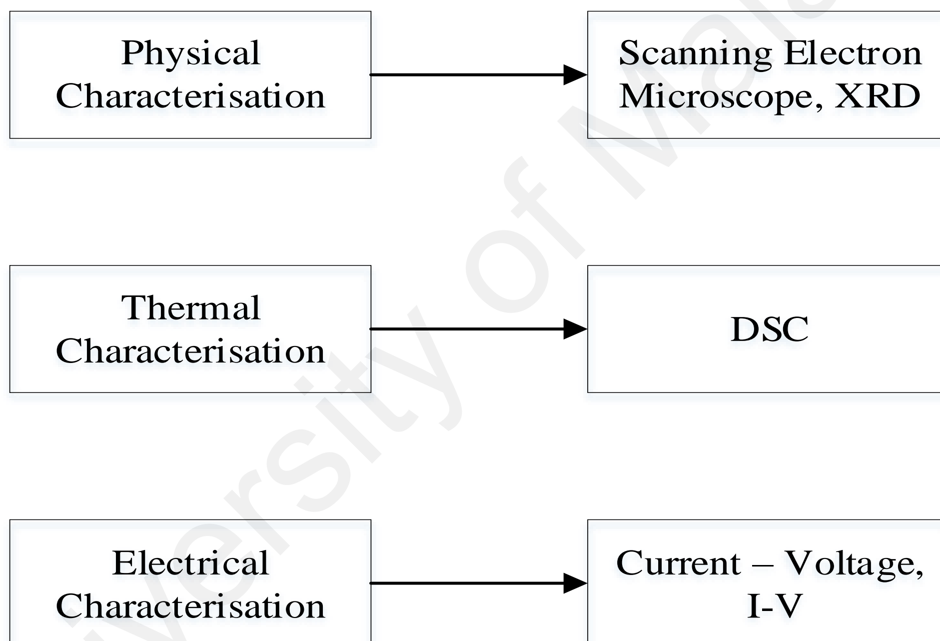

Figure 3.2: Characterization technique of Cu - Al nanopaste.

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3.2 Cu-Al Nanopaste Formulation Materials

The Cu-Al nanopaste was formulated using few chemical components which were categorized into material name, specification and supplier.

Table 3.1: Raw Materials that applied for Copper-Aluminium nanopaste formulation.

No.	Materials	Suppliers	Specifications
1	Cu powder nanoparticles	US Research Nanomaterial	Purity: 99.9%
2	Al powder nanoparticles	Aldrich	Purity: 99.5%
3	Terpineol	Aldrich	Electronic grade
4	Ethanol	Biotech Lab Supplies	95%
5	Resin binder,V006	Heraeus Inc. (USA)	25°C, 25-45 kcps
6	Ethylene Glycol	RiendemamSchmidt Chemical	M.Wt 62,07 g/mol

3.2.1 Cu-Al Nanopaste Formulation

The organic additives and also the metallic particles were mixed in order to formulate the Cu-Al nanoparticles according to the Table 3.1. The process involved was ultrasonic agitation. The Cu-Al nanopaste was formulated by underwent the ultrasonic agitation process in which copper and aluminium nanoparticles were mixed in ethylene glycol. The resin binder which was completely dissolved in terpineol was then mixed together with the solution which already prepared as before for the nanoparticles solution. All the mixture solution was stirred within two to three minutes in an ice bath where the temperature was controlled at 3-4°C. This ice bath stirring process was done with specific size of mechanical stirrer throughout the experiment conducted.

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Vacuum evaporation was carried out for the paste that obtained eventually in order to gain the necessary viscosity after the dispersion of organic additives as listed in Table 3.2. The weight of the EG, terpineol, and binder were fixed. The Al weight percentage was varied by using total nanoparticles loading which was 5.00 grams. The total nanoparticles included Al and Cu. The content for Al weight percent was varied within 20%, 40%, 60% and 80% in order to meet the objectives of this research project. High temperature applications is the reason for such loading of nanoparticles. Bai *et al*. (2006) stated that the variation in nanoparticles weight is exclusively crucial since the previous literature works have cautioned during sintering process for the inhibition use of solid-state reactions. The content for Al weight percent versus the content for Cu weight percent were then calculated and 4 set of samples were formulated for the research project experiment.

Table 3.2: Cu-Al die attach nanopaste formulation.

Set	Nanoparticles (g)	Al (g)	Cu (g)	Binder (g)	EG (g)	Terpineol (g)	Nanoparticles loading, %
1	5.00	1	4	0.05	0.50	0.20	87.0
2	5.00	2	3	0.05	0.50	0.20	87.0
3	5.00	3	2	0.05	0.50	0.20	87.0
4	5.00	4	1	0.05	0.50	0.20	87.0

The formulation process flow was depicted in Figure 3.3. The EG solution which include 10 ml of ethanol was added into the mixing of Cu and Al nanoparticles. The agitation process was then carried out ultrasonically in an ice bath within three minutes. The first layer which is coated is formed and the surface of nanoparticles would be enveloped by EG coating. The temperature in ice bath was kept between 4-5°C. As nanopaste formulation formed ethanol was not supplied in such process as it could be vaporized eventually in order to provide the good condition of nanopaste successfully. Binders was then dissolved using terpineol solution and added subsequently to the

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agitated nanoparticles solution previously. The stirring process was then carried out again about one to two minutes in an ice bath. The purpose of the binders was to form another coating layer which surrounded the ethylene glycol layer on the surface of nanoparticles. The final prepared solution was evaporated in vacuum to remove excess ethanol at 70°C for three hours.

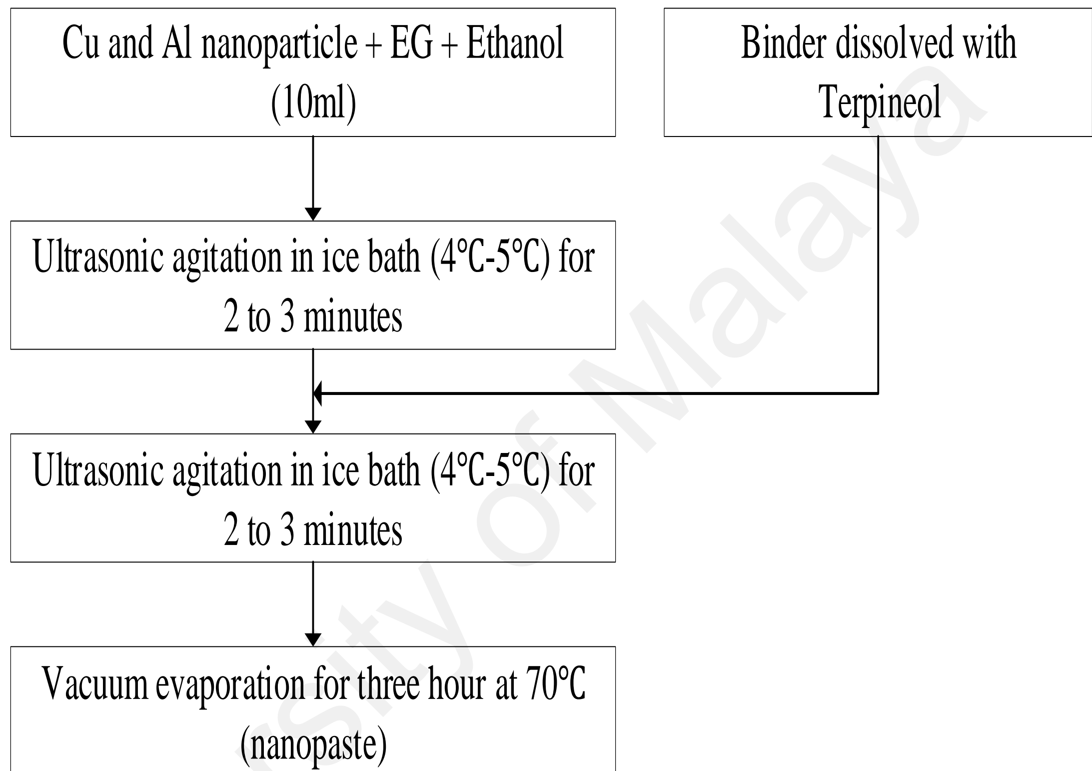

Figure 3.3: Process flow for Cu-Al die attach nanopaste formulation.

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3.2.2 Cu-Al Nanopaste Sintering

Copper-aluminium bonding nanopaste was then sintered by using a specialized brand horizontal tube furnace at 380 °C ± 10°C at a dwell time of 30 minutes in open air. The ramp rate was controlled at 5°C/min from room temperature up to the setting temperature. The temperature was chosen at 380°C was due to the TGA results which showed that all organic additives was burnt off at 380°C stated by (Manikam *et al*., 2012). As soon as the organic additives coating burnt off, a higher temperature was able to be avoided, oxidation of the die attach material's surface would take place, meaning the electrical properties and thermal properties were able to undergo degradation.

EDX analysis was performed on post-sintered Cu-Al nanopaste for 10-50 minutes and at 30 minutes, a sharp drop occurred for oxygen and this was due to the organic additives in the nanopaste are made up of oxygen as well as carbon molecular chain for particular long chain binder. The oxygen content increased after 30 minutes which was an indicator for the chemical process such as oxidation process of the nanopaste layer during phase transformation without liquefaction when most of the organic additives undergo rapid combustion. Such environment is especially crucial for nanopaste systems as this can determine whether the organic additives used were equally burnt off which also aids in the fusion and formation for nanoparticles. The presence of oxygen is extremely crucial due to the use of organic additives for example binders which the presence of carbon molecules (Hu *et al.*, 2010). The formulated Cu-Al nanopaste was sintered inside the chamber of the furnace in air exposure condition which means without the use and supplication of inert gas as shown in Figure 3.4. Such condition allowed more oxygen supply during the sintering process of Cu-Al nanopaste in order to burn off organic additives for the solid state fusion of Cu-Al nanopaste which aided in the coalescence of nanoparticles.

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Copper-aluminium nanopaste sample in quartz boat with horizontal shape tube furnace.

Figure 3.4: Experiment setup for sintering Cu-Al nanopaste in air gas flow.

The sintering condition with specific parameters as stated was proven had the ability to give a satisfied effect on the outcome of the nanopaste in which around 61.7% was able to be avoided for the defects such as under cured samples and also cracking samples. 30 minutes controlled for the dwell time able to burn off the nanopaste which make it brittle in nature.

3.3 Investigation of Physical, Electrical, and Thermal Characteristics for Cu-Al Nanopaste.

The thermal, electrical, and physical characteristics will be investigated for Cu-Al nanopaste in which the investigation verified the difference of Al weight percent content within Cu-Al nanopaste. The organic additives for weight percent content and total content for nanoparticles was fixed at 87.0%. The Al weight percent content in the Cu-Al nanopaste was varied from 20% to 80% as listed in Table 3.3.

Table 3.3: Samples for Cu-Al nanopaste for Al weight percentage variation content by having fixed nanoparticles content with total of organic additives weight percent content at 87.0%.

Sample No.	Cu-Al loading (wt%)
1.	Al 20-Cu 80
2.	Al 40-Cu 60
3.	Al 60-Cu 40
4.	Al 80-Cu 20

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3.3.1 Physical Characterization

3.3.1.1 Scanning Electron Microscope (SEM)

Scanning electron microscope was used in order to observe the morphology of the post-sintered Cu-Al die attach nanopaste. Electron microscopy can also be used to study the chemistry of the materials. Besides, it can also be used to evaluate the orientation of boundary grains. Crystallography information could be obtained from using this analyzer. In-situ experiments such as effects of temperature and reaction with atmosphere can be done through using such electron microscopy. This microscope is able to use for morphology purpose is due to the excellent magnitude in depth of focus. The larger the magnification, the better the resolution. Hot stage with excellent function is included in electron microscope together with other accessories. The principle in SEM involving the shooting of high power electron on the sample specimen and the electrons which ejected from the surface is then analyzed. The incoming electron beam which scattered on the sample either inelastically or elastically. After that, different signal can be detected and give alertness. The interaction volume is affected by the average atomic number as well as acceleration voltage. The electron sources from electron microscope involving secondary electrons, Auger electrons, and also backscattered electrons. Secondary electrons are produced due to the collision of high speed incoming electron which further eject the electron out of the shells. More than one electron will be produced for each incoming electron. As the incoming electrons enter the surface the secondary electrons type 1 are produced which will eject at higher angle and thus produce good resolution image. Incoming electrons which undergo few inelastic scattering and come close to the surface will provide secondary electron type two in which this type of secondary electron has higher surface area compared to the incoming electrons. Therefore, secondary electron type two has poor resolution image. The factors which affect the secondary

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electrons emission involving the surface condition, the atomic number, the beam energy and current, as well as topography which is the most crucial factor. Backscattered electrons are fraction of failure in electromagnetic field of the nucleus and if scattering angle is larger than 180°C, the electron will escape from the surface.

3.3.1.2 X-Ray Diffraction (XRD)

X-ray diffraction is produced from the atomic planes which caused the incident beam of X-rays which will interfere with one another as the rays emitted from the surface. XRD function included to measure the average spacing between layers of atoms (Noda *et al*., 2006). Besides that, XRD measures the orientation of a single grain and also the size of crystallize region. High speed electron collide with metal target will produce X-rays. The intensity of the peak is affected by the amount of substance. The relative of the amount of each components in the mixture is able to be measured in order to compare the peak intensity of the component in the mixture. The grains will not be oriented in common polycrystalline. In-situ study involved temperature, pressure and electronic field (Groza & Zavaliangos, 2003). Source of electrons are from the hot tungsten filament and the collision among anode, cathode and metal target for example copper and aluminium. It can also be used to study the crystal structure. Cu-$K_{\alpha 1}$ radiation which having the wavelength value of 3.6250 λ on a PANanalytical model was used which was carried out by XRD. The objective is to help in identification of sintered Cu-Al nanopaste.

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Thermal Characterization

Differential Scanning Calorimetry (DSC)

DSC was used to determine the melting point the samples. It is thermal analysis technique in which the amount of absorption and releasing of heat energy is measured. Solid samples was used to analyzed in order to provide the transition energy measurement at the transition temperature. Phase transformation were evaluated. Processing, thermal and mechanical properties were determined through differential scanning calorimetry and the effects of material were compared (Jiang & Wong, 2010). The steps involving included two pans sit on a pair which are connected to a furnace and the difference in energy either exothermic or endothermic reaction were recorded. Endothermic and exothermic reaction peaks are related to thermal events in the samples. The reversibility of the process was studied through heating followed by cooling process. The program software in computer generating the power supply for the pans in order to ensure there is the identical temperatures between the sample and the pan. Differential scanning calorimetry measures the change in heat of transitions. The degree of crystallinity and the degree of curing could also be determined. The area of differential scanning calorimetry could be divided into linear baseline, tangential area, and sigmoidal baseline. Linear baseline was suitable to be used for measurements in which there is no important modification in heat capacity during melting process (Tan & Cheong, 2014). The linear baseline was generally used. For tangential area baseline, the baseline was used when the melting process is affected by heat capacity change and also the sloping baseline was existed. Other than that, the baseline is used when the melting process is affected by heat capacity for sigmoidal baseline. Temperature on the peak point is not necessary corresponded to the melting temperature and the signal diminished slowly after the peak even though the samples were completely in molten state for such specific temperature.

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The specific heat capacity is measured as well as the total heat flow into the sample is measured as well. A range of thermal event involved glass transition temperature, DSC tests were conducted at a rate in which the output per minute is of 10°C/min from 30°C to 100°C in ambient atmosphere by using nitrogen purge using a Mettler Toledo 821 instrument system.

Electrical Characterization

Current-Voltage (*I-V*)

The Current-Voltage (*I-V*) measurements was performed using a computer controlled SPA system. Measurement approach used scanning photo thermal imaging as well as the frequency-domain electrical thermometry. The spatially die attach material resistance was extracted from the temperature rising at the surface during transient heating. The present work uses data for the resistance in order to get the image which is different from the previous photo thermal studies. The *I-V* curves were conducted and measured by using two probes technique. The *I-V* curve calculate the parameter in which the system included software, chuck and electronics with irradiance monitoring process. The *I-V* measurements were used to obtain the resistance, R, which is demonstrated in Equation 3.1 in which I is current while V is voltage.

$$R = \frac{V}{I} \tag{3.1}$$

The resistivity, ρ, was calculated from Equation 3.2, whereby L is length of the copper plate while A is the cross-section of the stencil printed area.

$$R = \frac{\rho L}{A} \tag{3.2}$$

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The electrical conductivity of the synthesized material was demonstrated from Equation 3.3, with σ represented electrical conductivity (Zhigal's skii and Jones, 2003).

$$\sigma = \frac{1}{\rho} \tag{3.3}$$

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CHAPTER 4: RESULTS AND DISCUSSION

4.1 XRD analysis

XRD Analysis for Sintered Cu-Al Nanopaste with Different Aluminium Weight Percentage Content.

Through the supplication of designed sintering conditions, the XRD analysis therefore proves that the silver and aluminium nanoparticles were able to disassemble together and form mass compound. The method which involved data collection required incident beam to be parallel with the beam of photos. The beam is needed to be assured so that the given photon beam will be absorbed strongly by the material. Phase transformation process of elements is utmost crucial. The bonding strength between the elements depends steadily on the completeness of rapid combustion of organics, which was shown to occur through EDX analysis. If the combustion process does not react completely or did not take place, it would act as a restraint for chemical bonding between the elements Ag and Al in the nanopaste (Bai *et al*., 2007c).

Sintering effects on the Ag_{80}–Al_{20} nanopaste material is important in helping for rapid combustion of organic in order to ensure the fusion of solid binding among the metal and element in the nanopaste (Bai *et al.*, 2007c). The higher number of Al_2O_3 peaks showed in diagram indicated to the ease at which ability of aluminium to undergo oxidation process, compared to Ag. Nanoparticles will undergo oxidation in high rate even in their pristine state without the supplication of heat treatment which is in contrast with the annealing process. This is particularly true for the metals which has the ability to sustain acid as shown in Figure 4.1 (Groza & Zavaliangos, 2003; Groza, 1999; Rellinghaus *et al*., 2001; Wang *et al.*, 2008; Noda *et al.*, 2006). The Al and Cu were analyzed using XRD analysis in which Al nanoparticles depicted peaks of diffraction at planes (111), (200), (220), (311) and (222), which is in compactible with face-centered-cubic (FCC) structures

whereas for Cu depicted peaks of diffraction at the planes of (111), (200), (220), and (311) and this conveyed that Cu is face-centered-cubic structure. Peaks for the Al_3Cu_2 hexagonal phase appeared at planes (111), (012), (004), (203), which corresponded reference file no. ICDS 98-005-7668. While for the $AlCu_3$ hexagonal phase appeared at planes (002) and (022) which corresponded reference file no. 98-015-0823. For AlCu the phase appeared at planes (301), (110), (411), (404), and (224). There is no aluminium oxide detected in the nanopaste. Sintering effects on the compound nanopaste is very important to help in organic burn off as well as to promote fusion in solid state among the metal and also elements (Bai *et al.*, 2007). The burn off temperature of the binder need to be in 380°C in which this is crucial for the sintering profile designed.

For CuO, the phase appeared at plane (111) which corresponded to ICDS file no. 00-005-0661 and 00-041-0254. Unreacted Al peaks were detected at plane (111) as stated in ICDS files No. 00-001-0176. The peaks of CuO were quite strong, indicating both elements did not react and oxidized when the organics burnt off. Homogeneous packing for particles of different sizes in nanopaste which were not entitled to pressure of any kind when undergo sintering process (Bai *et al.*, 2007c).

The burn off temperature of the binder need to be in 380°C in which this is crucial for the sintering profile designed. This scenario was controlled when a dual inlet system of inert gas and oxygen were used simultaneously. The reduction level on the sintered Al and Ag surfaces is resulted from the good controlling by the gas flow and duration in the chamber.

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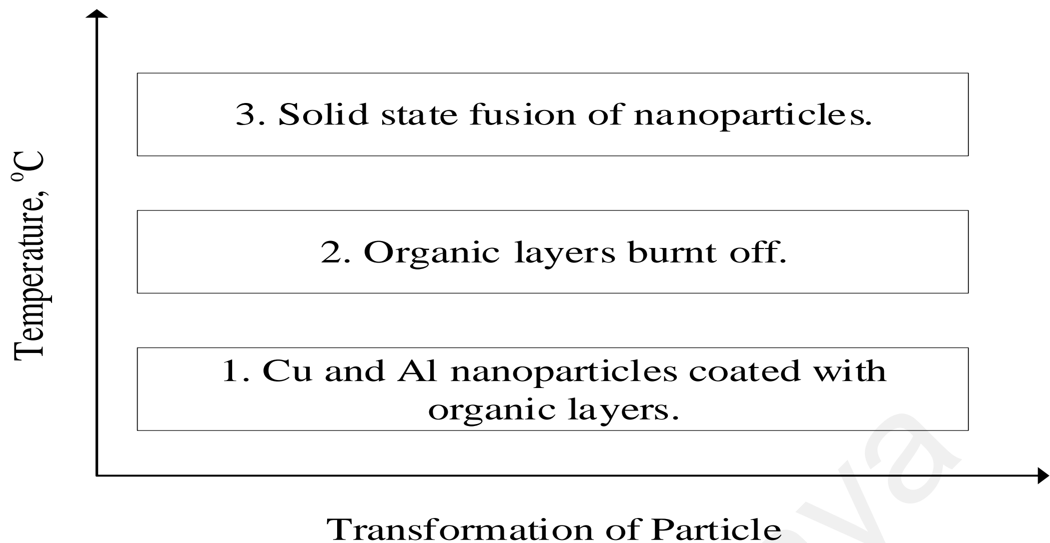

Figure 4.6: Organic nanoparticles layer burn off sequence during sintering ((Manikam *et al.*, 2013).

The rate of chemical binding between the metallic nanoparticles during sintering was needed to be enhanced and controlled in order to avoid the formation of oxides as the supplication of heat energy will generate vigorous oxidation process on nanoparticles as oxygen steals electron from another compound and change the appearance of the elements (Manikam *et al.*, 2013). High organic content will result in the formation of oxides and thus hinder the fusion of solid-state between elements of Al and Ag (Bai *et al.*, 2007c). Therefore, unreacted Cu will get oxidized as the sintering process goes on when exposed instead of forming compound. Optimum sintering profile used in manufacturing is absolutely crucial to support in solid state binding and joining between various metal elements in the nanopaste and to help in burnt off of organic. These four samples used has total 13.0% organics content (Manikam & Cheong, 2011). The expected level included efficiency of coalescence between Al and Cu able to meet required requirement (Manikam & Cheong, 2011). This is due to the organic additives burnt off and also oxidations from the surrounding are trade off factors. Organic residues are not able to remove completely, anyway, die attach materials falls between categories of nano-composite and alloy.

In a nutshell, the XRD analysis showed that the copper and aluminium nanoparticles were able to fuse and bonded by using the specifically designed transformation conditions in which the process did not involve liquefaction and without heat application. The binding between the elements is affected by the rapid combustion process and the level of rapid combustion for organic additives is determined was determined through how much solid-state binding fusion reactions took place between the Cu and Al nanoparticles. Incomplete coalescence of particles was observed which indicated that the mixing of these nanoparticles did not have been homogeneous agglomeration leading to aggregation might have occurred during the nanopaste sintering process.

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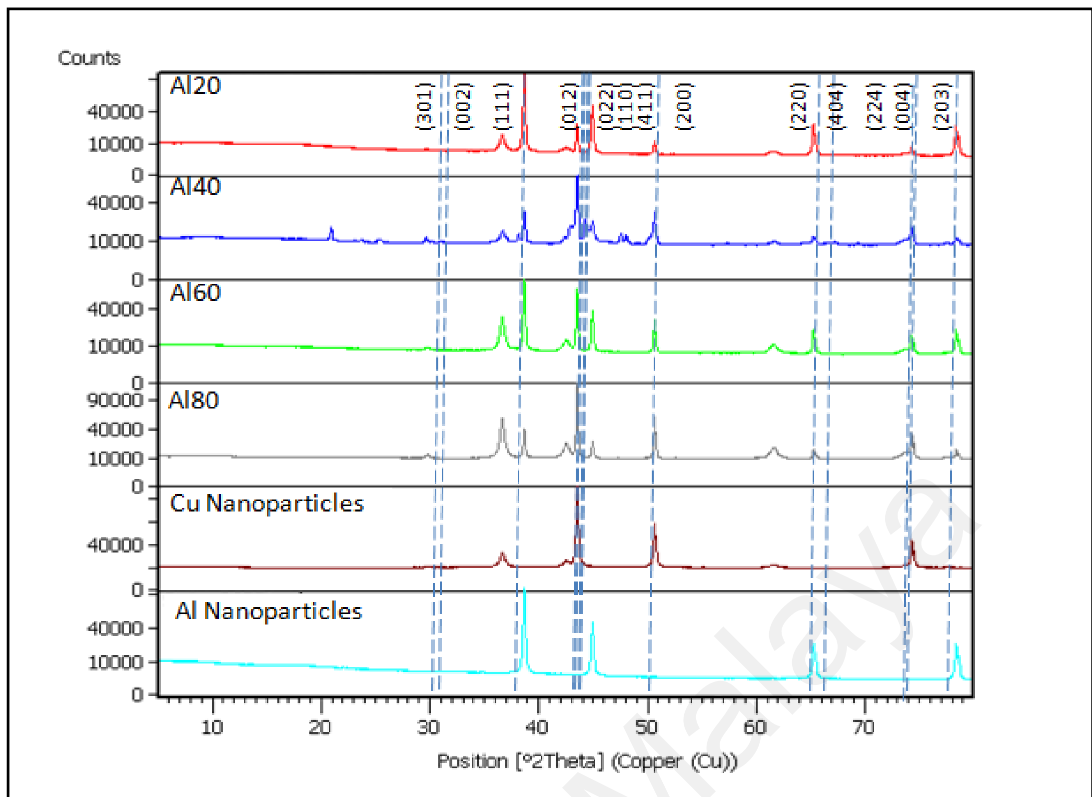

Figure 4.7: X-Ray Diffraction diagram for the pure Cu and Al nanoparticles as well as sintered Cu and Al nanopaste (87% weight percent nanoparticles content) with different Al weight percentage.

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4.2 DSC Analysis

DSC Identification of Post-Sintered Copper-Aluminium Nanopaste with Various Al Weight Percentage Content.

Post-sintered Cu-Al nanopaste samples with nanoparticles loadings 87.0% were identified and analyzed using differential scanning microscope to determine the melting points and characteristic of the samples was identified as well. When the sample undergo physical transformation heat was absorbed into the sample in order to maintain the temperature of reference material. The process was measured during the heating process. The melting point of the samples were determined for comparison due to the calorimetric measurements on the transition energy at transition temperature. The overlapped curves showed that the curves were transferred to higher endothermic heat flow with the addition of aluminium loading. There is the melting temperature of phase transformation showed for the apparent and sharp of endothermic peak which was revealed. Nonetheless, there is the restriction of the machine to perform the test up to maximum temperature of 1000°C. There is no change in the mass while there was change in thermal changes. Heat of It can be seen that all the post-sintered nanopaste samples represented melting point values undergo endothermic reaction which involving the absorption of heat. Compared to the melting point of Ag and Al nanopaste, the T_m of the bulk Cu and Al is higher (Bai *et al.*, 2007). The values were recorded in Table 4.1 for Cu-Al nanopaste along with the respective enthalpy of melting, **Δ**H. The Cu_{80}-Al_{20} has the highest melting point compared with other samples. From DSC analysis Cu and Al nanoparticles depicted at melting points of 256.90 ± 1 °C and 275.0 ± 1 °C, respectively which were taken at the onset of the plots. This phenomenon is coherent with the research that showed in which the Ag_{80}-Al_{20} alloy gives a melting point of approximately 800°C compared to the nanopaste samples which have lower melting point which is around 518°C (Northen *et al.*, 2007).

The depletion of the remaining liquid in aluminium and the liquid composition shifted toward the eutectic composition although alpha phase formed. Heat absorption occurred in order to achieve melting point of the sample. Additional heat is needed in order to increase temperature. Area of dip is the heat of melting. Physical changes involved endothermic reaction. There are melting, desorption, as well as vaporization. The remaining liquids follows the eutectic reaction when the composition reached eutectic condition. Binary Cu-Al solder alloy melted at a temperature lower than either of the two components. The melting temperature of Al was 224±1°C while Cu was 196±1°C. For eutectic solder of 40wt% Al melted at 234°C and 229 for 60 wt% Al and for 80 wt% Al nanopaste, it melted at 226°C.

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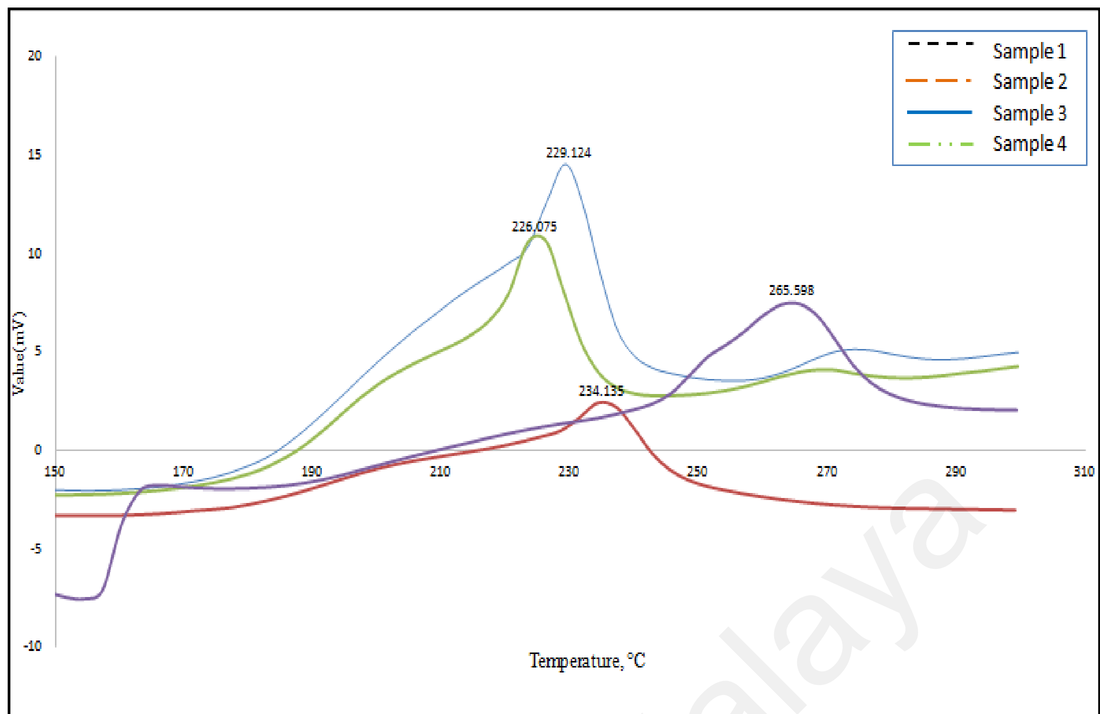

Figure 4.8: DSC plot for Cu-Al nanopaste having various nanopaste weight percent content sintered at 380°C.

The lower melting point for nanopastes is probably due to the organic content in which the organic additives affected the composition within the material itself during sintering process as well as the reaction with different nanoparticles. Carbon burnt off process also will affect the lowering of melting point and the ability rate of the organic material to evaporate at normal temperature increases when the sintering temperature increases. This resulted the organic molecules to search pathway to decamping from the nanopaste layers and the substance released as a form of gas. This condition will damage the formation of heavy materials which created a more permeable material and translated to larger surface areas (Northen *et al.*, 2007). Heat convection within the sintered nanopaste samples as well as the formation of pores contributed to the reduction of melting point. The first nanopaste sample which is Cu_{80}-Al_{20} undergo through phase transformation at 380°C in such caloric testing and with the increasing of aluminium percentage nanopaste formulation during sintering process the density will reduce due to the increased in formation of pores. Burnt off is another factor causing in this decreasing trend for melting point. The increased of permeable characteristic from the phase transformation synthesis

process resulted a huge effect of heat convection within the nanopaste sample and therefore it is very easy for the material to achieve a steady-state temperature during DSC analysis (Lafdi *et al.*, 2007). The melting point for the Cu_{80}-Al_{20} sintered samples were much higher compared to the bonding process of the die or the connection systems among nanoparticles. (Jiang *et al.*, 2007; Jiang *et al.*, 2008; Chen *et al.*, 1998). This demonstrated that the solid-state strong bonding adhesion between Cu and Al nanoparticles to form the Cu-Al nanoalloy involved immense vibration of molecules during the endothermic reaction which involve the absorption of energy from the reaction among inter-molecules and intra-molecules.

Table 4.1: Enthalpy of melting and melting point for Cu-Al nanopaste samples having different aluminium weight percent content.

Nanoparticle loading, %	Enthalpy of melting, J/g	Melting Point, °C
Cu_{80}-Al_{20}	59±1	265±1
Cu_{60}-Al_{40}	37±1	234±1
Cu_{40}-Al_{60}	18±1	229±1
Cu_{20}-Al_{80}	15±1	226±1

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4.3 Electrical Conductivity Measurements

Die-back metallization is exclusively crucial to form a good for non-rectifying electrical junction as well as to provide optimum surface conditions for die-attach materials. In order to pass mechanical, thermal and electrical requirements at high temperatures die back coating or to function as covering selection is exclusively needed. Al is chosen due to the price is cheaper compared to both Au and Ag since this would provide the characteristic as a candidate for application at high temperature due to the ability in providing adhesion strength after sintering process of the nanopaste. The electrical conductivity of the Cu-Al nanopaste increased with the increase of Al weight percentage content. There is the gradually increased in electrical conductivity which can be seen between samples by varying 20-80% Al weight content. The Cu_{20}-Al_{80} nanopaste sample has the highest value of electrical conductivity value among all the Cu-Al nanopaste samples at 1.0×10^4 (ohm-cm)$^{-1}$. As the Cu weight content increased to 80%, the electrical conductivity values significantly dropped to 1.09×10^{-6} (ohm-cm)$^{-1}$. Previous literature reported that Ag nanopaste gave an electrical conductivity value of approximately 2.64×10^5 (ohm-cm)$^{-1}$. The Ag_{80}-Al_{20} nanopaste fusion sample's electrical conductivity was 62% lower than that of the value of silver nanopaste. The ability of thermal conduction is strongly affected by the resistance of thermal at the die attachment due to the immense in rising of temperature in transistors which cause short life span of material produced. This is because due to the formation of CuO compound indicated that these elements did not react and oxidized when the organics burnt off. This is an oxidation phenomenon in which it maybe a case for the non-homogenous packing for particles of different sizes in a nanopaste. The formation of big dimension of the material is mainly due to the density weakness among particles. This was demonstrated through the formation of unoccupied space among the particles showed and therefore there is an issue termed partial delamination. The resistance of such electronic material affected seriously on the bonding property as well as experience for temperature

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of the electronic assembly. Besides that, there is a lot of data showed during the analysis for the materials thermal properties and this is suitable to predict the material resistance due to the forming of partial delamination in particles.

The selection of Al was proven in which the nanopaste systems was able to resist high temperature cycling tests and also to provide enough joint reliability especially in die-attach applications (Manikam & Cheong, 2011). Ag-Al die attach material was screen printed onto soda lime glass substrates and sintered using designed profile. As thermal aging repetitions increase, the electrical conductivity of Ag-Al die attach material fall slightly (Manikam & Cheong, 2011). It seemed to undergo a reduction in electrical performance as the die-attach material with high copper content. The reduction was mainly due to the electrical conductivity percentage in which the repetition for thermal aging increased. This was mainly due to the decomposition as well as volatility which caused necking other than grain growth (Manikam & Cheong, 2011). From SEM micrographs, the phenomenon was not clearly visible from SEM micrographs. In the nutshell, the overall performance of the die attach material was higher than that of epoxies which provided good conducting characteristic and low melting alloy systems. The results showed that Cu is a poor die back metal and this was due to the peeling seen on the failures. The trimming process was caused by the ease of Cu to be oxidized during the sintering which caused it to become brittle as well as detached from SiC die’s surface (Manikam & Cheong, 2011). The pores in the die-attach material is believed to cause the decrease in hardness and stiffness which showed a degradation in electrical conductivity. Binder concentrations on the sample surface were lower indicated high curing temperature which was preferred for binder molecules migration to the interface at high curing temperature. The mechanical shear strength which measured at room temperature of the dies material using the process was satisfactory while for temperature range indicated low as well as the stability of the resistance for die-attach was achieved.

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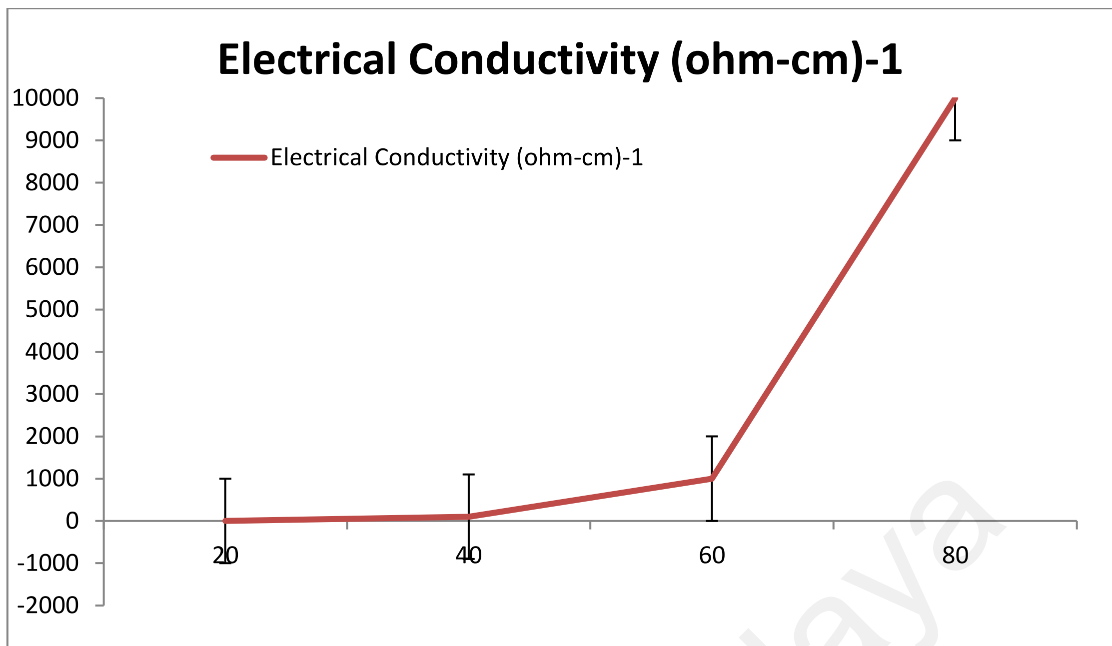

Figure 4.9: Error bar plot of electrical conductivity for Cu-Al nanopastes (87% weight percent content) with increasing Al weight percentage.

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4.4 SEM Microstructure Analysis of Cu-Al Nanopaste having Different Al Weight Percentage Content.

The microstructure transition for the Cu_{80}-Al_{20} material binding samples with different nanoparticles loading after sintering at 380°C. As the aluminium weight percent increased, the surface roughness of the binding material reduced. Larger grains were seen forming in the samples with high copper content. Larger percentage of copper consumed longer time to burn off during binding process and therefore can be attributed to the formation of the larger grain structures.

A mixture of Cu and Al nanoparticles content helped the formation of grain boundaries in which the orientation of crystal structure was identified. Besides that, the joining and formation of Cu and Al nanoparticles are able to form. A larger degree of permeable pores is formed due to the characteristic of the permeable pores of the organic additives during sintering in which it consists the ability in searching pathway from running away out of the surface layers and normally, they will escape in gas form (Durairaj *et al.*, 2009 & Siow, 2011). Durairaj *et al.* (2009) stated that it is widely known that an organometallic system in which chemical compound consists one chemical bond will specifically undergo three stages during phase transformation process. The first step is the breakable process of the organic additives, then followed by sintering which involving particle formation and joining, and finally is recrystallization involving slight dilation. The built up of carbonaceous contaminating films after the electron beam interact with irradiation of extended period. In this case, sufficient vacuum is needed to achieve stability of thermal and chemical property and the signal electron must travel from sample to detector in order to get the good resolution image. Besides, nanoparticles loading content affected size of grains. Signal overlapping caused defect in the analysis of the samples as well. Samples undergo SEM analysis was analyzed in three different modes included line scan,

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spot analysis, and mapping of chemical concentration. The Cu-Al nanopaste sample having 87% nanoparticles loading with 13.0% organics weight percent content sintered at 380°C and the change in microstructure was observed. As the Al content increased in nanopaste content, the microstructure changed from smaller grains to bigger one. The microstructure looked destroyed at 380°C in which it showed the importance of organic additives as it controls the densification of the materials during sintering process. There are considerations when using such analysis included signal to noise ratio. Besides that, dead time and the drifting of electron beams with time period. This can be shown through the size of grains.

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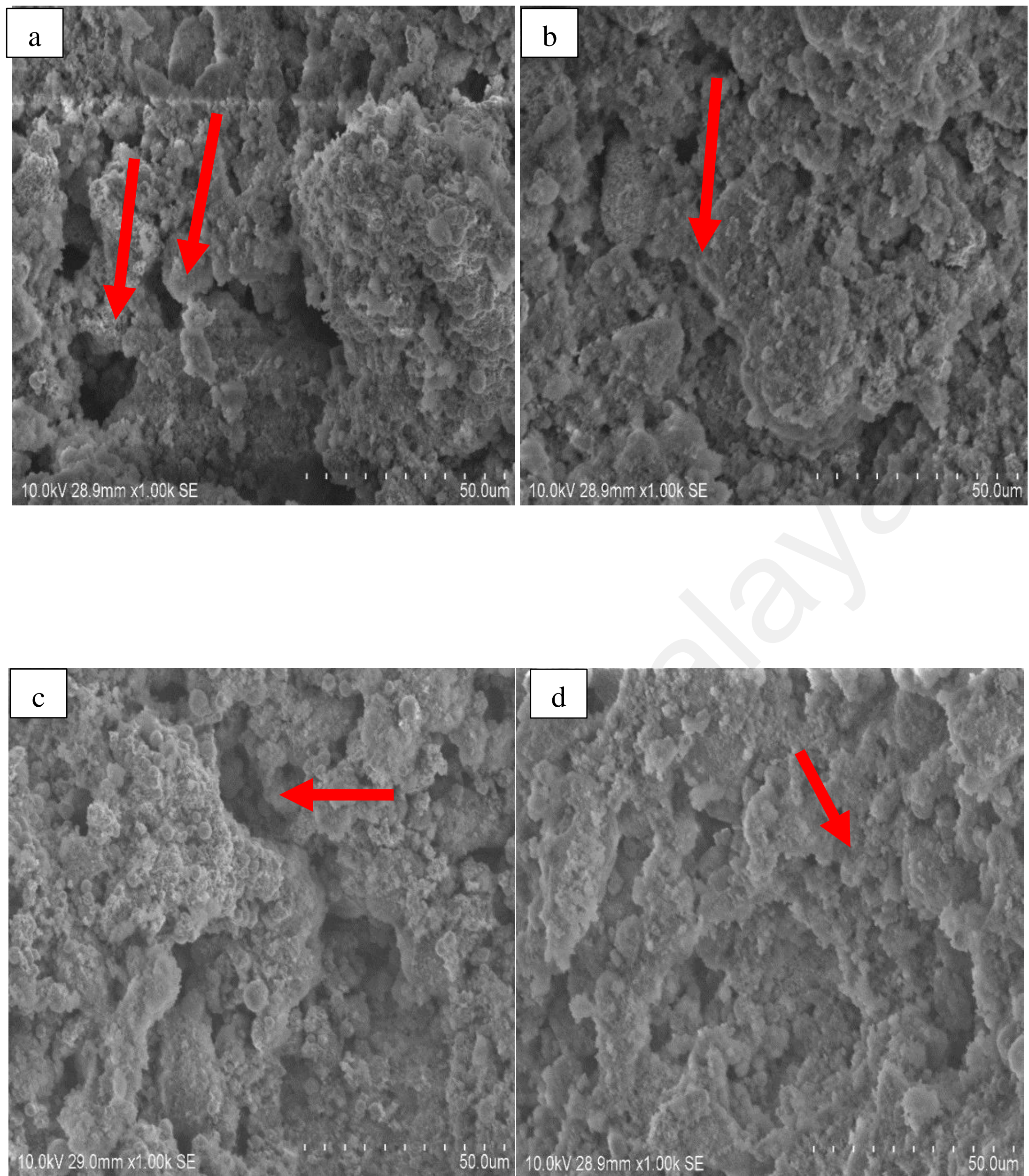

Figure 4.10: SEM image at 10,000× magnification of Cu_{80}-Al_{20} nanopaste (a), Cu_{60}-Al_{40} nanopaste (b), Cu_{40}-Al_{60} nanopaste (c), Cu_{20}-Al_{60} nanopaste (d).

The surface morphology of die attach material was observed. Formation of unoccupied space occurred frequently due to the rough or uneven surface morphology which is specifically for the applications of multiple stacking (Lee *et al.*, 2011). High surface roughness indicated that there is the formation of pores and also increased in electrical resistivity and this characteristic is not satisfied as well as not qualified for phase transformation material. Masson *et al.* (2011) stated that the formation of bigger grains from the results of particle agglomerations is a very fundamental step during solid-state fusion process in associated with organic additives burnt off transformation. These nanoparticles of metal and elements are not able to join and form the dense structures meaning there is the fully occupied of nanoparticles which is in contrast to the results showed. A more crystalline material formation was able to take place with less organics content according to Manikam and Cheong (2011). Surface morphology is extremely crucial as if the surface is smooth, larger grain will form and this is exclusively important for good thermal and electrical performances in high temperature bonding material. Besides this, formation of larger grains and coalescence of particles promoted the densification of the die attach material. The porosity and density for the nanopaste sample with different nanoparticle loading after sintered at 380°C were compared and this resulted in the porosity reduced as the aluminium content increased in the nanopaste samples. The reduction in porosity increased the density of nanopaste samples. The burn off of organics will resulted in the creation of pores and reduction in density since the formation of CuO existed in the samples as shown from XRD results. The burnt off of organics take longer time to burn off and therefore created more pores and this made up larger surface area within nanopaste itself. Therefore, it can be concluded that the adjustment in sintering temperature is exclusively important in order to achieve a greater hardness and density so that the good characteristics of the material is able to be optimized.

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CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The copper-aluminium nanopaste sintered at 380°C in air were formulated using organic additives. Such burnt off temperature help in a solid state reaction between the copper and aluminium nanoparticles in which their melting point were 196±1°C and 224±1°C. The Cu_{20}-Al_{80} nanopaste sample showed the lowest melting point compared to others. A huge heat convection within nanopaste sample was encountered which is resulted from large pores causing high melting points in Cu_{80}-Al_{20} samples. Enthalpy of melting point in nanopaste sample showed highest for Cu_{80}-Al_{20} nanopaste samples. Therefore, the sintering temperature was suitable to create solid state reaction. Solid state reaction required energy absorption which involved endothermic reaction. Such reaction occurred through the rapid evaporation of ethylene glycol due to high temperature during sintering process as the binder layers burnt off. The dwell time was set at 30 minutes while for the ramp rate was set at 5°C/min respectively. A larger percentage of pores represented a drop in the enthalpy of melting. $AlCu_3$ and Al_3Cu_2 compound were detected in XRD diffractogram from the organic additives burnt off. CuO compound formation was basically from the oxidation process. This happened through nanopaste layer during sintering process when organic additives burnt off especially the oxygen content increased after 30 minutes. Oxygen from air is extremely crucial to help in the copper-aluminium nanopaste solid state fusion. Since there is the Cu-Al compound showed in XRD diffractogram therefore it can be concluded that there was the connection within the die attach material and this can be further proceeds with the analysis of electrical performances.

With the increasing of aluminium weight percent content, the electrical properties increased gradually. The top value for electrical conductivity obtained for the Cu_{20}-Al_{80}

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die attach nanopaste was 1×10^4 $(\text{ohm-cm})^{-1}$ respectively. These values were less compared to silver-aluminium die attach material which is comparable with high temperature die attach solder alloys as well as epoxy-based adhesives. Copper-aluminium die attach system has presented average electrical properties which are suitable to be used as high temperature die attach material.

The microstructure of the nanopaste showed the formation of big grains and structure as nanoparticle content in which aluminium content increased from 20% to 80%. The increasing in density as the Cu-Al nanopaste underwent sintering process can be shown through the SEM results in which there is the obvious of porosity formed in the samples. Incomplete coalescence of particles was observed which showed that the mixing of these nanoparticles were not been agglomerated as well as non-homogeneous which resulted in aggregation of nanopaste which might have occurred during the nanopaste sintering process.

The porosity behavior did affect in electrical conductivity in which the higher the porosity in the sample, the lower the electrical conductivity due to the failure in heat convection. The porous samples can achieve steady state temperature among all the samples tested. The nanopaste sample showed promising electrical conductivity results for high aluminium content sample and therefore, aluminium proved to be a good metal.

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5.2 Recommendations

Microwave irradiation process can be considered as an alternative technique to replace sintering process. This is possible in increasing the surface area of the compound and therefore grain growth can be achieved in die-attach material in order to optimize the densification process as well as to achieve time saving. Besides that, metallic-oxide solutions is suggested to use in order to decompose the release oxygen molecules. This is to avoid the formation of oxide compound and also to ensure the organic additives to burn off more completely in order to allow decomposition to take place for the formation of nanoalloy through the fusion of solid-state reactions.

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