OPTIMIZATION OF SILVER NANOPARTICLES SIZES IN Ag-Cu NANOPASTE AS DIE-ATTACH MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

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by

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LIST OF ABBREVIATIONS

ACA	Anisotropic conductive adhesive
AFM	Atomic force microscopy
CTE	Coefficient of thermal expansion
DSC	Differential scanning calorimetry
EG	Ethylene glycol
FESEM	Field emission scanning electron microscopy
HRTEM	High resolution transmission electron microscopy
ICA	Isotropic conductive adhesive
ICSD	Inorganic crystal structure database
LFA	Laser flash analysis
MEMS	Micro-electro-mechanical system
PVA	Polyvinyl alcohol
RMS	Root-mean-square
SAC	Sn-Ag-Cu
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

α	Coefficient of thermal expansion
at%	Atomic percentage
ΔT	Change of Temperature
M	Performance Index
^{o}C	Degree Celsius
MPa	Mega Pascal
MV/cm	Megavolts per centimeter
min	Minute
cm	Centimeter
cm/s	Centimeter per second
nm	Nanometer
µm	Micrometer
eV	Electronvolt
I	Current
s	Second
Ω	Ohm
$(\Omega.cm)^{-1}$	Ohm per centimeter
%	Percentage
σ	Conductivity
t	Thickness
V	Voltage
W/cm-K	Watts per centimeter-Kelvin
wt%	Weight percentage

PENGOPTIMUMAN SAIZ ARGENTUM NANOPARTIKEL DALAM NANOPES Ag-Cu SEBAGAI BAHAN LAMPIR-DAI UNTUK APLIKASI SUHU TINGGI

ABSTRAK

Peranti elektronik yang digunakan untuk suhu tinggi lampau (>500^{o}C) sebagai contoh dalam aplikasi penerbangan dan aeroangkasa, terus menjadi permintaan. Nanopes Ag-Cu ialah campuran nanopartikel Ag dan Cu dengan penambah organik (pengikat PVA, etilena glikol), telah diperkenalkan sebagai teknik lekapan dai. Dengan menggunakan nanopartikel, keperluan untuk tekanan luar ketika proses pensinteran telah dihapuskan dan suhu pensinteran boleh dikurangkan dengan menggunakan pengikat PVA, yang mempunyai suhu penguraian lebih rendah (280^{o}C) apabila dibandingkan dengan pengikat komersial V-006A (380^{o}C). Dalam kajian ini, nanopes Ag-Cu dengan sebanyak 0.15 g pengikat PVA disejatkan selama 30 min, memaparkan nilai keberalian elektrik 3.26 x $10^5(\Omega.cm)^{-1}$ pada 340^{o}C suhu pensinteran optimum dan 5^{o}C/min kadar pemanasan. Kajian diteruskan dengan menggabungkan pelbagai saiz Ag nanopartikel pada sifat elektrikal, haba dan mekanikal, Set II (150 + 20-50 nm) masing-masing memaparkan nilai keberaliran elektrik dan haba paling tinggi iaitu 1.15 x $10^5(\Omega.cm)^{-1}$ dan 143-181 W/m-K. Namun, nilai kekuatan ricih untuk Set II hanya 0.78 MPa. Kajian tentang sifat mekanikal nanopes Ag-Cu menggunakan pengikat berlainan (pengikat komersial V-006A) yang direkodkan adalah 12.05 MPa pada 260^{o}C suhu pensinteran optimum dan 5^{o}C/min kadar pemanasan. Kesimpulannya, saiz Ag nanopartikel (150 + 20-50 nm) menawarkan nilai keberaliran elektrik dan haba yang baik sebagai bahan lampir-dai untuk aplikasi suhu tinggi.

OPTIMIZATION OF SILVER NANOPARTICLES SIZES IN Ag-Cu NANOPASTE AS DIE-ATTACH MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

ABSTRACT

Electronic devices used for extreme high temperature (>500^{o}C) for instance in aviation and aerospace applications, continue to be in demand. Ag-Cu nanopaste, which is a mixture of Ag and Cu nanoparticles and organic additives (PVA binder, Ethylene glycol), has been introduced as die attachment technique. By using nanoparticles, the need of external pressure during sintering process is eliminated and the sintering temperature can be reduced by using PVA binder, which has lower burn-off temperature (280^{o}C) as compared to commercial binder V-006A (380^{o}C). In this study, Ag-Cu nanopaste with 0.15 g amount of PVA evaporated at 30 min, displays electrical conductivity value of 3.26 x $10^{5}(\Omega.cm)^{-1}$ at 340^{o}C optimum sintering temperature and 5^{o}C/min heating rate. Further investigation on the combination Ag nanoparticle sizes on electrical, thermal and mechanical properties shows that Set II (150 + 20-50 nm) displays highest electrical and thermal conductivity value, which is 1.15x $10^{5}(\Omega.cm)^{-1}$and 143-181 W/m-K, respectively. However, the shear strength value for Set II is only 0.78 MPa. The mechanical properties of Ag-Cu nanopaste using different binder (commercial binder V-006A) were studied and the bonding attributes recorded is 12.05 MPa at optimum 260^{o}C sintering temperature and 5^{o}C/min heating rate, which is not comparable to the mechanical properties of Ag-Cu nanopaste using PVA binder. In conclusion, Ag nanoparticle sizes (150 + 20-50 nm) offered good electrical and thermal conductivity value as die-attach material for high-temperature applications.

CHAPTER ONE
INTRODUCTION

1.1 Theoretical background

High temperature electronic devices are widely used in numerous applications, for instance in automotive, oil and gas, and aircraft industry(Chin *et al.*, 2010). These industries require electronic devices that are capable to withstand extreme high temperature (>500^{o}C) and on the same time, reliable. Therefore, the reliability of these devices is vital to ensure their performance.

SiC-based electronic devices can be operated efficiently at temperatures beyond 600^{o}C due to its wide band gap properties (Chin *et al.*, 2010). In fact, this important attribute has overcome the limitation of low operation temperature (<250^{o}C) for conventional silicon (Si)-based electronic devices. Hence, the challenge to develop electronic devicesthat comparable to SiC-based is continue to rise. To address this issue, the development of electronic packaging particularly in die-attach technology is being researched. This is due to the fact that the reliability and overall functioning of these electronic devices depends on the die-attach quality in the first level electronic packaging.

A die-attach material should ideally demonstrate a melting temperature that is higher than 500^{o}C, in order to operate in high-temperature environment. Besides, the die-attach material should be able to have low processing temperature as well. In addition, another criteria required are good electrical and thermal conductivity, and acceptable bonding strength.

1.2 Problem statement

As Si-based electronic devices can no longer meet the requirement of high operating temperature, SiC-based electronic devices have been developed specifically to overcome the issue (Manikam and Cheong, 2011). As a vital part of electronic package, die-attach materials not only provides an electrical interconnection and mechanical fixation between a die and a substrate but also create a path for heat generated by semiconductor to dissipate as well (Abtew and Selvaduray, 2000; Lu *et al.*, 2004).

Therefore, the challenge to seek a die-attach material that can be operated at high temperature (>500^{o}C) is continue to rise. For instance, conductive adhesive, conductive glass and Bismuth (Bi) solder alloys are only suitable for low-temperature range of applications due to their low melting temperature (Gao *et al.*, 2014; Lahokallio *et al.*, 2014; Kisiel and Szczepański, 2009; Wang *et al.*, 2014; Spinelli *et al.*, 2014). On the other hand, gold-nickel (Au-Ni) solder alloy offers high melting point of 980^{o}C, but its high soldering temperature has become a drawback to fulfill the die-attach material requirement.

To overcome the limitation in high processing temperature, new die-attachment technique has been introduced, namely metal film and metal paste. These two aforementioned techniques utilize the inter-diffusion bonding of metal film and sintering process to form intermetallic compounds, which acts as a joint between die and substrate (Mustain *et al.*, 2010; Chuang and Lee, 2002; Kähler *et al.*, 2012; Zhang and Lu, 2002). As for metal paste, raw metal with high melting temperature such as Au formed a homogenous inter-metal layer with application of external pressure (0.28-0.55 MPa) upon sintering process (Mustain *et al.,* 2010). The same technique is applied for silver (Ag) and copper (Cu) micropaste that an external pressure of 40 MPa is applied during sintering process and the sintering temperature has reduced to 250^{o}C (Kähler *et al.*, 2012; Zhang and Lu, 2002). Nevertheless, the application of pressure during bonding process is unfavorable because it could complicate the manufacturing process.

To address the issue, a strategy of reducing the size of metal particles in metal paste to nanoscale (nanopaste) has been introduced. The reduction of particle size is aim to increase the chemical driving force of metallic particle and thus, eliminate the need of external pressure application. The pressure-less sintering process for Ag nanopaste could be attained in open air at a temperature of 280-300^{o}C with 40 min dwell time (Bai *et al.*, 2007; Bai *et al.*, 2006). Positive results were obtained for Ag nanopaste which is good electrical conductivity value of 2.5-2.6 x 10^{5} $(\Omega.cm)^{-1}$, and grain growth occurred during sintering thus createa microstructure consisted of a dense network with micrometer-size pores(Bai *et al.,* 2006).Despite the great qualities, Ag nanopaste is limited to its high cost, which is critical for mass production.

Hence, silver-aluminum (Ag-Al) nanopaste is introduced to overcome the limitations of Ag nanopaste. Ag-Al nanopaste does only cheaper in cost, it can also be sintered at 380^{o}C in open air ambient (Manikam *et al.*, 2013a;Manikam *et al.*, 2013b; Manikam *et al.*, 2013c; Manikam *et al.*, 2012a; Manikam *et al.*, 2012b). In addition, the Ag–Al nanopaste with 84.7-87.0% nanoparticle loading offered an electrical conductivity value range from 0.95 to 1.01x 10^5 $(\Omega.cm)^{-1}$ (Manikam *et al.*, 2013a). Even though the electrical conductivity value for Ag-Al nanopaste is higher than Sn, Bi, Au and Zn solder alloys [0.02-0.71x 10^5 $(\Omega.cm)^{-1}$], it is still lower than the electrical conductivity value for Ag micropaste [4.17 x 10^5 $(\Omega.cm)^{-1}$]and Ag nanopaste [2.50-2.60 x 10^5 $(\Omega.cm)^{-1}$] (Bai *et al.*, 2006, Kähler *et al.*, 2012, Zhang and Lu, 2002).

Cu was chosen to replace Al in Ag-based nanopaste because it has the second best electrical and thermal conductivities among other metals, and low-cost. In fact,the standard electrode potential of Cu is closer to Ag which will eliminates the risk of galvanic corrosion (Chawla, 1993).Due to aforementioned qualities, Ag-Cu nanopaste is introduced and it could be sintered in open air at temperature of 380^oC similar to Ag-Al nanopaste (Tan and Cheong, 2013). Ag-Cu nanopaste with various loading offers electrical conductivity range from 0.81 to 2.27 x 10^5 $(\Omega.cm)^{-1}$ (Tan and Cheong, 2014a; Tan *et al.*, 2014b). The electrical conductivity of Ag-Cu nanopaste is notably higher when sintered at open air ambient other than nitrogen and argon ambient [1.78-1.85x 10^5 $(\Omega.cm)^{-1}$](Tan and Cheong, 2013;Tan and Cheong, 2014a; Tan *et al.*, 2014b).

In this work, an attempt to lower down the sintering temperature of Ag-Cu nanopaste (380^oC) by using organic additive with lower burn-off temperature will be investigated. The Ag-Cu nanopaste is formulated by mixing Ag and Cu nanoparticles with organic binder, polyvinyl alcohol (PVA). The study covers determination of optimum amount of PVA binder, drying time and sintering temperature of Ag-Cu nanopaste. Further investigation on physical and electrical properties of Ag-Cu nanopaste at various sintering temperatures will be discussed. Next, effects of combined Ag nanoparticle sizes on physical, electrical, thermal and mechanical properties of Ag-Cu nanopaste will be discussed. In this particular study, only the amounts of Ag nanoparticles are varied, while the size and amount of Cu nanoparticles is maintained. Lastly, bonding attributes of Ag-Cu nanopaste formulated by commercial V-006A binder at various sintering temperatures and heating rates will be discussed.

1.3 Research objectives

The primary aim of this research is to develop Ag-Cu nanopaste that can be sintered at low processing temperature without the application of external pressure, and fulfill the requirements for high-temperature die-attach properties. In order to achieve the primary objectives, the optimization of Ag-Cu nanopaste were systematically investigated as listed below:

1. To optimize Ag-Cu nanopaste by mixing similar size Ag and Cu nanoparticles (50-60 nm) with organic binder (PVA).
2. To investigate the properties of Ag-Cu nanopaste bycombining three sets of Ag nanoparticle sizes (20-50, 50-60 and 150 nm), while maintaining the size and amount of Cu nanoparticles (50-60 nm).
3. To study the effect of different binder (commercial V-006A binder) on thebonding attributes of Ag-Cu nanopaste.

1.4 Scope of study

The structure of this research work is divided into three parts. In the first part, Ag-Cu nanopaste was formulated by mixing Ag and Cu nanoparticles with various loading of PVA binder and organic additives. The stencil printable quality of Ag-Cu nanopaste will determine the optimum amount of PVA. Various drying time and sintering temperature were used with the intention to obtain and optimize the sintering condition. The physical and electrical properties of Ag-Cu nanopaste (PVA binder) at various sintering temperatures were investigated. In the second part, three sets of combined Ag nanoparticle sizes in Ag-Cu nanopaste was prepared to study its effects on physical, electrical, thermal and mechanical properties of Ag-Cu nanopaste (PVA binder). In the last part, bonding attributes of Ag-Cu nanopaste formulated by V-006A binder at various sintering temperatures and heating rates were investigated.

Various characterization techniques were used in this work and they are categorized into physical, electrical, thermal and mechanical characterizations. For physical characterization, field emission scanning electron microscopy (FE-SEM), polarizing microscope, high resolution transmission electron microscope (HR-TEM) and atomic force microscopy (AFM) was used to observe the morphology and surface topography of sintered Ag-Cu nanopaste. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) was carried out to identify phases presented in the sintered Ag-Cu nanopaste. For electrical characterization, four-point probe was used to calculate the electrical conductivity value. For thermal characterization, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was used to determine the burn-off temperature of organic additives and sintered Ag-Cu nanopaste. Thermal conductivity was obtained by using laser flash analysis. For mechanical characterization, bonding strength of Ag-Cu nanopaste was determined using lap shear test performed by Instron universal testing machine.

1.5 Thesis outline

This thesis is divided into 5 chapters. Chapter 1 provides an overview of high-temperature electronic packaging, followed by the challenges in the development of high-temperature die-attach material, research objectives, and scope of study. Chapter 2 covers the literature review and background theories in the study. Chapter 3 presents the materials and detailed methodology steps that employed in this research. Chapter 4 focuses on the results and discussions of the findings. Lastly, Chapter 5 summarizes the overall findings of this study and suggestions for future works.

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

Over the years, the demands for high-temperature electronic devices has increase significantly from various industry, such as oil and gas industry, aviation, aerospace, and automotive(Chin *et al.*, 2010). The electronic devices fabricated using silicon carbide (SiC) can be operated efficiently at temperatures beyond 600^{o}C, due to its wide band gap properties (Chin *et al.*, 2010). This important attribute has overcome the limitation of low operation temperature (<250^{o}C) for conventional silicon (Si)-based electronic devices. Nowadays, electronic packaging that offer comparable attributes to SiC-based electronic device are being developed to fulfill the demands. This chapter begins by reviewing the evolution of electronic device from Si-based to SiC-based, followed by their applications. The chapter will next cover an overview of electronic packaging and the materials used for high-temperature applications. For die-attach material, the basic requirements of a die-attach material, and its detailed literatures for high-temperature die-attach materials will be covered. In this thesis, the primary focus is on die-attach material specifically metal paste using metallic nanoparticles; hence, the characterization and properties of the die-attach materials will be presented.