SYNTHESIS OF GRAPHITE TO GRAPHENE BY MODIFIED ELECTROCHEMICAL EXFOLIATION METHOD TOWARDS ENHANCED THERMAL INTERFACE MATERIAL FOR HEAT SINK APPLICATION

by

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This work is dedicated especially to my beautiful kids.

Hopefully, it will inspire them to be far better than me...in everything.

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LIST OF ABBREVIATIONS

$(NH)_2SO_4$	Ammonium sulphate
CAMCs	Carbon Matrix Composites
CNTs	Carbon Nanotubes
CVD	Chemical Vapour Deposition
FC-PGA	Flip-Chip Pin-Grid Array
FESEM	Field Emission Scanning Electron Microscope
FETs	Field-Effect Transistors
FTIR	Fourier Transform Infrared Spectroscopy
GNPs	Graphene Nanoplatelets
GO	Graphite Oxide
HMDS	Hexamethyldisilane
HOPG	Highly Oriented Pyrolytic Graphite
HRTEM	High-Resolution Transmission Electron Microscopy
LCVD	Laser Chemical Vapour Deposition
LEDs	Light-Emitting Diodes
MCHS	Microchannel Heat Sink
MgO	Magnesium Oxide
MLG	Multilayer Graphene
MPCVD	Microwave Plasma Chemical Vapour Deposition
MPFL	Mechanically Pumped Fluid Loop
MWCNTs	Multi-Walled Carbon Nanotubes
$NaBH_4$	Sodium Borohydride
NMP	N-Methyl-2-Pyrrolidone
NMR	Nuclear Magnetic Resonance
PFHS	Pin-Fin Heat Sinks
PIV	Particle Image Velocimetry
RANS	Reynolds-Averaged Navier-Stokes
rGO	Reduced Graphene Oxide
rPE-CVD	Plasma-Enhanced Chemical Vapor Deposition
SCs	Solar Cells
SEM	Scanning Electron Microscope
SiO_2	Silicon Dioxide

SR	Graphene-Silver
TIM	Thermal Interface Material
TO	Topology Optimization
VACNTs	Vertically-Aligned Carbon Nanotubes
XPS	X-Ray Photoelectron Spectroscopy

LIST OF SYMBOLS

k	Thermal conductivity (W/m.K)
h	Heat transfer coefficient ($W/m^2.K$)
h_{ave}	Average heat transfer coefficient ($W/m^2.K$)
A_T	Total Area (m^2)
L	Length (m)
Q	Power (W)
R	Thermal resistance ($^oC/W$)
T_s	Surface temperature (^oK)
T_∞	Surrounding temperature (^oK)

Sintesis Grafit ke Grafene dengan Kaedah Pengelupasan Elektrokimia ke arah Bahan Antara Muka Termal yang dipertingkatkan untuk Aplikasi Sinki Haba

ABSTRAK

Pada masa kini, bekalan kuasa kepada sinki haba meningkat dengan ketara. Kajian pemindahan haba pada sinki haba adalah penting untuk memastikan bahawa jangka hayat, kebolehpercayaan dan prestasi sinki haba adalah lebih tinggi. Objektif utama penyelidikan ini adalah untuk mengurangkan suhu persimpangan sinki haba dengan menggunakan bahan antara muka termal yang juga dikenali sebagai pad haba. Bahan yang digunakan di pad haba mesti mempunyai kekonduksian terma yang tinggi dan rintanganterhadap haba. Oleh sebab itu graphene digunakan sebagai bahan utama di dalam penyelidikan ini bagi menggantikan beberapa bahan lain yang telah sedia ada. Komposisi graphene dikaji dengan mendalam bagi mengetahui kesan terhadap kekonduksian terma bagi mendapatkan kekonduksian terma yang optima. Proses sintesis dilakukan dengan menggunakan kaedah-kaedah pengelupasan elektrokimia kerana caranya mudah dantidak memerlukan kos yang tinggi berbanding dengan kaedah yang lain. Sebaik sahaja penghasilan graphene dilakukan ianya dijadikan sebagai bahan antara muka terma. Bahan antara muka terma yang diperbuat daripada graphene akan dibandingkan dengan bahan antara muka terma yang sedia ada dari segi kekonduksian terma. Dalam kajian ini, kesan komposisi graphene sangat mempengaruhi nilai kekonduksian terma, dimana semakin tinggi nilai komposisi graphene yang digunakan semakin tinggi nilai kekonduksian terma. Kemudian, simulasi dilakukan menggunakan perisian Ansys-Fluent bagi mendapatkan nilai suhu bagi heat sink dengan menggunakan parameter yang sama dengan keadaan sebenar. Daripada keputusan, ia menunjukkan bahawa suhu sinki haba yang menggunakan bahan antara muka terma yang diperbuat dari graphene berjaya mengurangkan suhu sebanyak 20 hingga 40 %. Peningkatan kuasa yang dibekalkan kepada sinki haba dan juga cip menyebabkan suhu meningkat kepada 95.6 ºC pada 10 Watt,namun dengan menggunakan bahan antara muka terma yang diperbuat dari graphene berjaya mengurangkan suhu sehingga 62.4 ºC. Pengurangan suhu yang tinggi ini mampu mengelakkan komponen elektronik terutamanya sinki haba menjadi sangat panas dan juga rosak. Selain itu, bahan antara muka terma yang diperbuat dari graphene juga telah membuktikan ianya mempunyai kekonduksian terma yang paling tinggi dan baik berbanding dengan bahan antara muka terma yang lain. Peningkatan sebanyak 20 hingga 60 % di dalam kekonduksian terma menyebabkan ianya merupakan bahan antara muka terma yang terbaik untuk digunakan dalam mengurangkan suhu sinki haba. Kajian ini dapat mengoptimumkan prestasi dan kecekapan pad haba dengan menggunakan pad termal pada komposisi yang terbaik bagi menghasilkan bahan antara muka terma yang mana ianya dikaji dari 10 wt. % hingga 100 wt. %. Kepentingan kajian ini akan membantu para pereka elektronik membuat keputusan mengenai komposisi optimum yang boleh digunakan dan pada masa yang sama mampu memaksimumkan kebolehpercayaan dan ketahanan sinki haba.

Synthesis of Graphite to Graphene by Electrochemical Exfoliation Method toward Enhanced Thermal Interface Material for Heat Sink Application

ABSTRACT

Today, heat sink power source has increased significantly for many applications. The study of heat transfer in heat sink is important to ensure that the life expectancy, reliability and performance of the heat sink are higher. The main objective of this research is to reduce the temperature of the heat sink junction by using a thermal interface material, also known as a heating pad. The material used in the heat pad must have high thermal conductivity and heat resistance. Therefore, graphene is used as the main filler material in this research to replace some of the existing materials. The composition of graphene is studied in-depth to determine the effect of thermal conductivity to obtain optimum thermal conductivity. The synthesis process is carried out using the modified electrochemical exfoliation method because it is simple and does not cost much compared to the other methods. Once the graphene production is done, it becomes a thermal interface material. Thermal interface material made of graphene will be compared to existing thermal interface material in terms of thermal conductivity. In this study, the effect of graphene composition greatly influenced the thermal conductivity value, the higher the value of the graphene composition used, the higher the thermal conductivity value. Then, the simulation was performed using Ansys-Fleunt software to obtain the temperature value of the heat sink using the same parameters as the actual conditions. From the results, it is shown that the heat sink temperature using the thermal interface material made from graphene successfully reduced the temperature by 20 to 40 %. The increase in power supplied to the heat sink as well as the chip caused the temperature to rise to 95.6 ºC at 10 Watt but using a thermal interface material made of graphene reduced the temperature to 62.4 ºC. This high-temperature reduction can prevent electronic components, especially heat sinks from becoming very hot and damaged. In addition, the thermal interface material made of graphene has also been shown to have the highest thermal conductivity compared to other thermal interface materials. The 20 to 60 % increase in thermal conductivity makes it the best thermal interface material to be used in reducing temperature to heat sinks. Material which is studied from 10 wt. % up to 100 wt. %. The importance of this study is to help electronic designers decide on the optimum composition that can be used while at the same time, maximizing the reliability and durability of the heat sink.

CHAPTER 1 : INTRODUCTION

1.1 Overview

Thermal management is covering various forms of heat transfer, including conduction, convection and radiation, involving different processes especially in electronic industries. Thermal management in the electronics industry has become crucial, especially in removing the heat flux generated from the chip to the heat sink (Ansari & Kim, 2018; Moore & Shi, 2014). Heat transfer investigation for heat sink continues to be an important part for electronic devices. Increasing high level of performance in electronic devices demands more efficient thermal management system. Low thermal conductivity (thermal glue/ silicon elastomer/ rubber) causes heat sink or electronic devices to overheat and malfunction. One of the biggest problems is the high thermal contact between two surfaces under high heat flux which can affect the reliability of heat sink from overheating and malfunctioning (Drummond et al., 2018a; Kelly et al.,2018). There are a lot of countermeasures and research that has been done to solve the existing problems. The high thermal conductive material is one of the possible solution to solve the thermal management issue and to reduce thermal distribution of heat sink however depress the reliability of electronic components (Fang et al., 2018; Huang et al., 2018; Yuan et al., 2018). Thermal Interface Material (TIM) was proposed to improve the reliability and thermal conductivity of electronic components, especially in heat sink and chips application (Due & Robinson, 2013). Investigation of thermal interface material also focuses on reducing the thermal contact resistance between heat sink and chip to reduce the heat flux generated from chip to heat sink (Ryu et al., 2018). The traditional method to produce thermal interface material is usually using polymer (silicone elastomer) or grease due to its low thermal conductivity of TIMs (Huang et al., 2018; Mehra et al., 2018).

1.2 Problem Statement

Nowadays, heat transfer investigation for heat sink continues to be an important part for electronic devices (Ji et al., 2017; Kanargi et al., 2017; Tari & Mehrtash, 2013). The parameters such as the type of phase change materials, coolant systems, design of heat sink are important in the thermal management (Al-damook & Alkasmoul, 2018; Hajmohammadi et al., 2018; Hasan & Tbena, 2018). The conventional method in producing heat sinks typically uses copper as the main material. The main problem that occurs when using copper as the main material for a heat sink is that copper cannot disperse heat very well and has less resistance to high temperature (Jeng & Tzeng, 2014; Jeng, 2015). Hence, the thermal interface material is used to solve the problem of the excessive heat of heat sink and was able to reduce the temperature of heat sink by up to 30 to 40 % (Hajmohammadi & Toghraei, 2018; Ozsipahi et al., 2018). One of the most important properties in selecting thermal interface material to cool electronic devices is thermal conductivity (Wang et al., 2018). High thermal conductive material is used as thermal interface material to reduce the excessive heat transfer from the heat sink. Thermal grease and thermal paste are the most common types of high thermal conductive material used currently in the market (Yu et al., 2015). The base material in thermal grease and thermal paste is generally categorized as silicone or non-silicone type. This types of material uses silicone-based pastes because they are well-established, low-cost, high performing, and very reliable (Wang et al., 2014). The filler material in most pastes is metal oxide (ZnO, BN, and Al_2O_3), silver, or graphite. In order to increase the thermal conductivity, several high thermal conductive material has been used as a filler such as Cu, Al, AIN etc. (Chen et al., 2018; Nisar et al., 2018; Weiyuan & Wenjiang, 2013; Zhang et al., 2018). However, adding these fillers as much as 30 to 50 % of Cu, Al, AIN did not give much improvement to the thermal conductivity of the thermal interface material; it only increased up to 1-5 W/(mK) at room temperature (Ohashi et al., 2005). Besides that, there are also other problems caused by the use of thermal grease and thermal conductive adhesive such as overflow, inconsistent thickness and requires a curing process (Yu et al., 2015). However, after the discovery of graphene (3000 - 5000 W/mK) at room temperature which has the highest thermal conductivity compared to Cu (385.0 W/mK), Al (205.0 W/mK), AIN (285.0 W/mK), many researchers started to study the effect of filling graphene to the thermal interface material; starting with the study of composite between thermal grease with a small portion of graphene. It was then proven that thermal grease fill with 4.25 wt. % graphene was able to increase 668 % thermal conductivity up to 1.047 W/mK from 0.156 W/mK (Yu et al., 2014). Graphene sheets and alumina particles filler also were used to improve thermal conductivity. Graphene 1 wt. % was added in thermal grease to increase the thermal conductivity up to 3.45 W/mK (Yu et al., 2015). Epoxy has been incorporated with graphene to increase the thermal conductivity because epoxy has poor thermal conductivity (0.15– 0.25 W/mK) (Yuan et al., 2016). Epoxy are the important material as a binder material to bind together graphene as a filler. Thermal conductivity of thermal interface material increases up to 6.45 W/mK when it was incorporated with epoxy resin with 25 wt. % of graphene (Yu et al., 2007). In this research, the influences of graphene weight percentage on thermal conductivity are important to study in order to have the highest thermal conductivity in producing thermal interface material.

1.3 Objective

1. To synthesize graphene from graphite by using modified electrochemical exfoliation method with ammonium sulphate $(NH4)_2SO_4$ electrolyte at different exfoliation time and using sonication dispersing in N-Methyl-2-pyrrolidone (NMP) solvent.

2. Consequently, to produce a thermal interface material from the synthesized graphene for heat sink application.

3. To optimize the heat transfer of the heat sink using Ansys-Fluent software.

4. To optimize the graphene thermal conductivity through morphological study of the thermal interface material.

1.4 Scope of Research

In this study, modified electrochemical exfoliation of graphite (EEG) used graphite electrodes in forms of foils, rods or sheets or highly oriented pyrolytic graphite (HOPG). EEG can be carried out by using graphite as the anode and an aqueous electrolyte, which typically consists of acids (for example, H_2SO_4, H_3PO_4) or inorganic salts (Na_2SO_4, $(NH_4)_2SO_4$, K_2SO_4). The properties of the graphene sheets obtained by EEG depend on the type of electrolyte and its concentration, in addition to the characteristics of the starting graphite and operation conditions used in the EEG process, such as electrolysis time or voltage. Ion intercalations are expected to be influenced by graphite electrodes, microstructures, such as graphite particulate sizes, defects, layer arrangements, and thickness, composition, and suitable pre-treatment.

Optimization of the thermal interface material, the model will be used to investigate the heat transfer of heat sink using higher power output (up to 10 Watt). There are numerous types of thermal interface materials (graphene, graphite, CNT, GNP and AIN)), power source (1 Watt to 10 Watt) and several operation conditions (dimensions, size, thermal conductivity and heat sources) must be defined during the process to ensure that the results are accurate and acceptable. The type of materials of the heat sink (Cu) and the thermal interface material including graphene, graphite, CNT, GNP and AIN were used to improve heat dissipation and hence, reducing the junction temperature of the heat sink. Lastly, to optimize the findings and results, the composition (starting from 10 wt.% up to 100 wt.% of graphene) and the morphology of the thermal interface material were analysed to find the most suitable and effective composition of the thermal interface material. The numerical and experimental setup using several parameters like the type of thermal interface material used (graphene, graphite, CNT, GNP and AIN), different chips power (1 Watt to 10 Watt) used, the material of the heat sink and the material composition of thermal interface material used are very important in order to make sure that our results are accurate and acceptable.

1.5 Significance of study

The significant of the research are as listed below:

1. Able to synthesize graphene from graphite by using modified electrochemical exfoliation method using ammonium sulphate $(NH4)_2SO_4$ electrolyte at different in exfoliation time, which the process is a novel method and none had succeeded.

2. Thermal interface material was made from synthesize graphene using modified direct liquid-phase exfoliation method (to improve the purity and thermal conductivity of graphene) and then compared with other TIMs in order to find which TIM have the highest thermal conductivity.

3. For optimum thermal conductivity, the composition of graphene is between several fractions (10% wt. – 100% wt.)

4. Thermal interface material made from graphene can be applied to heat sinks in order to avoid the heat sink from overheating and malfunctioning.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

The purpose of this chapter is to provide a thorough review of the current and past works of thermal management of heat sink in electronic applications. Initially, a brief overview of the experimental and the numerical studies via Ansys-Fluent to solve the thermal management of heat sink problem are also brought into the limelight. There is also a brief review on the thermal performance of a two-layered stacked microchannel heat sink, cooling system of heat sink, modification of the design of heat sink, and high-thermal conductive material. In this chapter the highlighted technique is to synthesis and produce graphene by using Chemical Vapour Deposition (CVD) and chemically derived graphene method.

2.2 Thermal Management of Heat Sink

Advances in the field of electronics have resulted in a significant increase in power input, high performance and emerging trend of miniaturization of modern electronics. This resulted in dissipation of high heat flux at chip-level, heat sink and other electronic components (Drummond et al., 2018a; Han et al., 2018). In order to improve the performance and reliability of heat sink, improvements in cooling technologies are required (El-Adl et al., 2018). As a result, thermal management is becoming important and increasingly critical to the electronics industry. Thermal management is the controlling and monitoring action on heat dissipation and temperature fluctuations. The main task of maintaining an acceptable junction temperature by dissipating the heat from integrated circuit chips and heat sinks is a significant challenge to thermal engineers (Takács et al., 2017). However, the physical means associated with enhancing computing capabilities at the electronic component have also created a very challenging set of circumstances for keeping electronic devices cool, a critical factor in determining their speed, efficiency, and reliability (Alghoul et al., 2018; Moore & Shi, 2014). Natural convection cooling is advantageous for low power dissipation of heat sink since it offers a low-cost, energy-free, and noise-free operation (Sahoo et al., 2016). The thermal analysis have been done to solve the problems of thermal performance, low power dissipation of heat sink and high operational cost of testing which are by using experiment methods (Tang et al., 2018).

2.2.1 The Two-layered Stacked Microchannel Heat Sink

The design of the double-layer microchannel heat sink is one of the options to reduce not only the overall thermal resistance of the heat sink but also the maximum temperature differences on the bottom wall as compared to the original design (Leng et al., 2015). By increasing the number of layers in microchannel, thermal resistance was found to be decreasing with increasing channel depth and increasing mass flux while the heat sink with the smallest channel depth results in the highest heat transfer coefficients. It also results in the highest thermal resistance due to the significantly reduced wetted area in comparison to the deeper channels (Drummond et al., 2018a). However, by increasing the number of channels in the heat sink, or its size, is required to operate by using bigger pump size and power sources (Shen et al., 2017).