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Evaluation of High Thermal Conductivity - Sintered Hybrid Die-Attach Materials in High-Power Electronic Packaging and Interconnections: A Comprehensive Review

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ABSTRACT

In recent times, high-temperature applications are quite essential. However, most of the pure conductive materials that are currently available in the market are incapable of achieving high thermal conductivity. As a result, numerous researchers have investigated and tested a proper material process. Research on developing composite material such as hybrid silver with different particle sizes, silver/copper, silver/graphene, and copper/graphene are intensively discovered. Colloidal silver (silver organic) provides the highest thermal conductivity (229 W/m K) followed by hybrid graphene/copper material e.g., 168.5 W/m K. As the hybrid graphene/copper shows the positive impact in thermal conductivity, hybrid graphene/silver with two different sizes of silver particles has become an attractive option to be investigated. Thermal conductivity outcomes higher than 250 W/m K are expected to be developed.

Keywords: Thermal conductivity, composite material**,** hybrid silver, hybrid graphene/copper, hybrid graphene/silver

1. INTRODUCTION

Graphene is an innovative technology that truly has a big potential to improve an existing material and in a transformational capacity which could open up new markets and even replace existing technologies or materials. Biomedical [1-2], composite and coating [3], electronics [4–5], energy [6], membranes [7] and sensors [8-9] are a substantial range of industries that graphene could make a great impact. Graphene-based technology is rapidly improving since its first discovery in 2004 due to its unique structure and geometry which offers outstanding physical-chemical properties, including a high fracture strength, excellent electrical and thermal conductivity, fast-mobility of charge carriers, large specific surface area, and biocompatibility [10-11]. Graphene family nano-materials (GFNs) consists of single-layer graphene, bi-layer graphene, multilayer graphene, graphene oxide (GO), reduced graphene oxide (rGO) and chemically modified graphene which can be differentiated from each other member in term of oxygen content, the number of layers, surface chemistry, purity, lateral dimensions, defect density and composition [11].

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To date, electronic paste development has attracted extensive attention as the demand increases rapidly in the electronic industry. Electronic paste or usually known as the conductive paste is very important in manufacturing electrical devices e.g., flexible, and stretchable electronics, and electronic packaging and interconnections [12-16]. Previously, materials like conductive polymers [17-18], metal nanoparticles [19-21], carbon nanotubes, and graphene [22-25] are commonly used in the development of electronic paste. Polymer-based material has low thermal stability and poor conductivity than metallic materials [26]. Conventional conductive filler like Au and Pt has excellent conductivities but is too expensive for mass production and the reserve content is low which limits the further application [27-29]. Other than that, copper and aluminum metal have promising electrical conductivity but are easily oxidized which could affect the paste performance.

While silver material becomes the most preferable metallic material as it provides excellent electrical conductivity and good chemical stability. However, it has low electromigration resistance and is still expensive for large-scale applications in some cases. Carbon conductive paste-like CNT [30] and graphene [31-33] paste have limitations in poor dispersibility. Moreover, conventional carbon-based materials have low conductivity compared to metal as the carbon-based performance is affected by the chemical structure and quality of the material. As described before, each filler or conductive material exhibits several pros and cons, thus intensive research regarding the development of composite material for electronic paste has become an interesting field to explore especially in high thermal purposes. Therefore, the hybridization process with several types of conductive materials or the same materials but different particles shape is often to be investigated. Thus, newly developed hybrid materials with excellent properties will be utilized to overcome the limitation and preserve the benefit of the materials.

Currently, the high thermal conductivity of die-attach has become a key technological challenge as a high-power semiconductor as one of the highest growth sectors in the semiconductor industry. To meet this urgent requirement, composite die-attach sintering has emerged as a promising method for high-power applications. A large volume of published studies related to composite materials has been conducted in which could be a useful reference to develop a new sintered die-attach with high thermal conductivity. [34] hybridized two different sizes of Ag e.g., micron-sized Ag particles and submicron-sized Ag particles for low-temperature and low-pressure die-attach material. Other researchers revealed that micrometer flake shape Ag particles could self-generate silver nanoparticles during the sintering process and provides higher shear strength compared to the sub-micrometer spherical shape of Ag particles [35]. Moreover, as proposed by [36-37], nanocomposites of graphene and silver materials were synthesized by mixing graphene oxide (GO) with silver acetate and silver nitrate, respectively. Both researchers used thermal reduction and chemical reduction for the reduction process, respectively. As a result, silver nanoparticles synthesized on RGO nanosheet act like a spacer to prevent the RGO sheets from agglomerating which could improve electrical and thermal performances.

This paper intended to describe and discuss in detail about the die-attach sintering composite material. A clear understanding of the development of the sintered die-attach including fabrication process of paste, method of applying the paste, and sintering process will be reviewed. Then, the main characterization such as thermal conductivity is discussed as well. Finally, the advantage of graphene-based die attach material and future expectations/suggestions of high thermal conductivity (TC) in die-attach technology will be explained in the end of the paper.

2. DEVELOPMENT OF DIE-ATTACH MATERIAL

Die-attach materials are the materials that perform die bonding between the semiconductor and some substrate or semiconductor to its package. Other than that, it is used to attach electrical components, and in some cases, it can be used as a conductive line e.g., for flexible substrate application. In semiconductor application, die-attach materials function as a heat sink for the produced heat in the die, mechanical fixation of the die on the substrate, and electrical connection between the die and its package. Due to these functions, the thermal characteristic is critical to be included in the discussion and other factors such as pressure/pressure-less processes and sintering temperature should be taken into consideration. It is because, high pressure and sintering temperature can cause die cracking and heat stress effect, respectively.

2.1 Fabrication of Paste

Silver and copper and commonly chosen for die-attach material as those materials offer high melting temperature and high electrical conductivity. [34] hybridized two different sizes of Ag e.g., micron-sized Ag particles and submicron-sized Ag particles for low-temperature and low-pressure die-attach material. Two kinds of Ag particles e.g., flake particles (diameter, d: 8μm and 0.3μm) were mixed with two types of solvents, ethanol and ethylene glycol with the 12 % wt of solvent to ensure a suitable viscosity for screen printing at around 20,000 MPa. The hybridization effect of micron-sized and submicron-sized Ag particles in ethanol shows a slightly lower resistivity as compared to the paste with ethylene glycol e.g., 3.9×10^{-6} Ω cm and ~6.5×10^{-6} Ω cm, respectively. In addition, at a sintering temperature of 200 ^{0}C, sintered hybrid Ag paste possesses a high thermal conductivity of 140 W/m K for the single layer of hybrid paste on a soda-lime glass sheet [34].

[38] prepared nano-silver paste by formulating silver nanoparticles (300nm), succinic acid, ethanol, and a variety of organic solvents (alpha-terpineol, water-free alcohol, and polyethylene glycol 40,000) mixture by using stirring, centrifugation, ultrasonication processes. The silver nano paste was ball-milled for 48 hours using a ball mill with the ratio of silver nano paste to organic solvent of 7:3. The silver nano paste is used for the application of transparent electrodes via electric-field-driven micro-scale 3D printing [38]. Other researchers investigated a novel solvent micron-sized Ag paste for power semiconductor applications. Two types of Ag particles e.g., micron flakes (diameter, d: 8.0 μm, thickness, t: 260 nm) and sub-micron (d: 0.3 μm) particles were mixed with a new solvent composed of 4-(tert-butyl) cyclohexyl acetate as a dilute agent and HPMDA as a thickener using a hybrid mixer. Two types of Ag paste i.e., 94 wt% with new solvent and 90 wt% with ethylene glycol (EG) as controlled formulation were printed on soda-lime glass sheets using a screen printer, and Ag pastes were sandwiched between two Ag-plated Cu using stencil printing [39].

Both researchers that investigated the performance of low temperature and pressure of sintering process highlighted the solvent of paste as the main concern. The choice of suitable solvent in fabricating die-attach paste is a crucial aspect that needs to be taken into consideration as the characteristic of solvent ensures the excellent conductivity and high joint strength in die-attach technologies. Low temperature and low pressure/pressure-less in sintering give relatively advantages in reducing production costs. However, thermal conductivity is not clearly discussed in the publications related to the use of pure metal or alloy. According to Wiedemann-Franz Law, for both pure metal and alloy, the electrical and thermal conductivities are reduced by the same factor. The thermal conductivity is directly proportional to the electrical conductivity which will be explained in detail in the next topic.

Apart from focusing on the development of die-attach solvent, other researchers claimed that silver-based paste requires an intermediate layer between the paste and substrate to improve the joint interconnection. The additional metallization layer e.g., Ag and Au coated on the Cu substrate is widely used in power electronics. However, this method needs extra raw materials and processing steps which will increase the cost [40-42]. Research of low-cost hybrid Ag paste containing micron-scale Ag flakes and submicron-scale Ag spheres on a bare Cu substrate was investigated by [43]. Equal weight of micron and submicron-scale Ag particles were dispersed together in ethanol and a hot plate was used to evaporate the mixture into uniform dry powder at 45 °C. 10 % wt of mixture powder was mixed with CELTOL-IA solvent using a hybrid mixer to produce Ag paste and was applied using a stencil printer to attach Cu dummy chip on Cu substrate [43].

Other researchers synthesized colloidal silver using Carey Lea's method which citrates dense layer on Ag nanoparticles (13 nm) surface became the organic shell of the sol. Two different organic shell thicknesses were modified, e.g., thin, and thick with the ratio of organic content to Ag of 2.5: 97.5 and 7.6: 92.4, respectively. The colloidal silver paste was dispersed in $NaNO_3$ in order to thin the organic shell and centrifuged to obtain the Ag paste. Thin organic shell showed the highest thermal conductivity as high as 229 W/m·K which was higher than half bulk conductivity of Ag (410 W/m·K) [44].

Other than silver, copper is one of the significant metals in the industry due to its excellent thermal and electrical conductivities. However, their instability against oxidation under an ambient condition and the formation of Cu oxides, such as cuprous oxide (Cu_2O) and cupric oxide (CuO) during the heating process become the main challenges. [45] investigated copper as a die-attach material by evaluating the performance of three different mixtures of copper paste. One spherical-shaped copper powder and two flake-shaped powders with 3.6 µm and 3.3 µm each, were prepared. 75 % wt of Cu was mixed with the organic solvent, and the milling process was used to ensure a better dispersion. The results revealed that flake shape can create a Cu joint compared to a spherical shape. The copper oxidation is the main challenge that needs to be improved as Cu oxide can be observed at the outer edges of copper strips. An insufficient nitrogen flow during the sintering or cooling process led to the copper oxidation [45].

The combination of Cu and Ag as the composite paste is expected to surpass the previous limitations of Ag and Cu nano-paste which could lower the cost especially for Ag materials and simplifying the die-attach sintering process e.g., sintering in an air atmosphere without the assistance of external pressure and additional annealing step. Ag (40 ± 10 nm) and Cu (50 ± 10 nm) were mixed with an organic binder (resin binder) and solvent (terpineol and ethylene glycol) to develop Ag/Cu nano-paste. 87 % wt of combination Ag and Cu was mixed with binder and solvent with various amounts of Cu e.g., 20, 40, 50, 60 to 80 wt% with respect to Ag content. The 20 % wt of Cu in sintered AgCu paste demonstrates the best combination of thermal conductivity which is 159 W/m K and shows the declining trend of thermal expansion coefficient when the amount of Cu increases in combination paste [46].

Recently, the performance of sintered copper by adding graphene/Cu–Cu_xO with sintered pure copper (≤100 nm) was compared in the study conducted by [47]. Thermal performance as well as electrical and mechanical performances of the thermal interface material (TIM) were improved as the C–O–Cu bonds formed at the interface between graphene (1–3 layers, 8–12 µm in length/width) and copper nanoparticles. A schematic diagram of the hybridization process between Cu–Cu_xO nanoparticles on plasma-treated graphene (PTG) is shown in Figure 1. Surface treatment using oxygen plasma of graphene was performed prior to the chemical bonding with copper acetate. The thermal reaction between treated graphene and copper acetate synthesized copper nanoparticles on treated graphene surface after sonication, hot plate stirring (90 °C), and annealing in a vacuum furnace for 1 hour (450 °C). In addition, for conductive paste preparation, oxide-free copper nano-powder was then mixed into graphene/copper composite and organic solvent including n-butanol and terpineol to produce sintered DA materials. The appearance of graphene reduces the interfacial thermal resistance between graphene and copper which improves the thermal conductivity of copper matrix up to 123.5 % as compared to oxide-free copper paste e.g., 168.5 W/m K and 75.4 W/m, respectively [47].

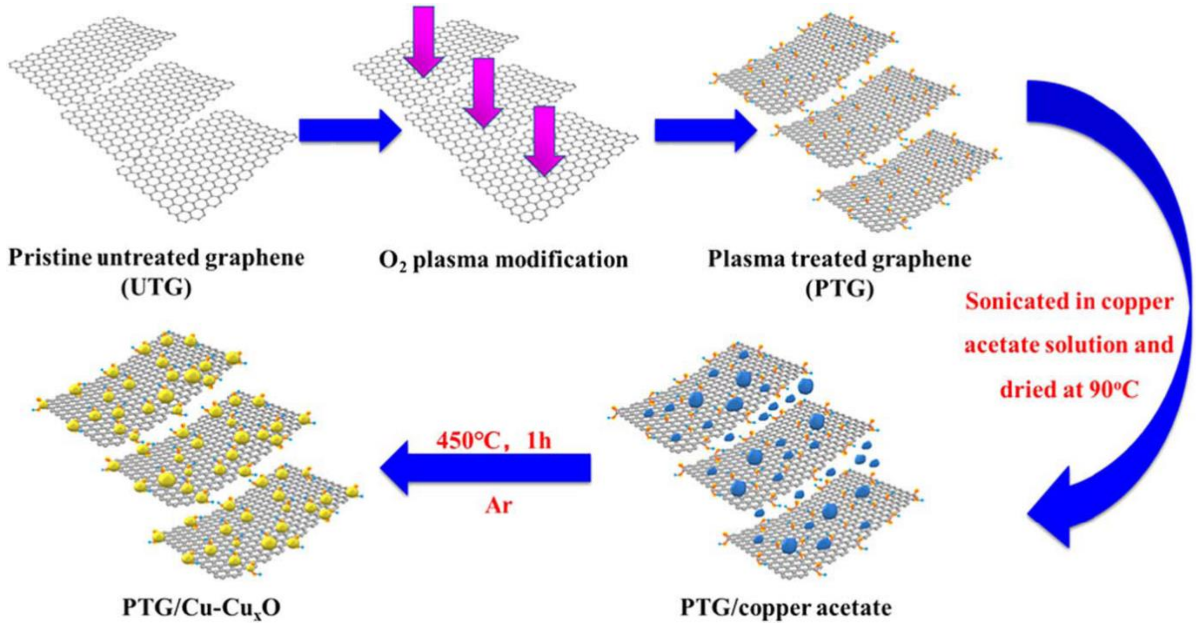

Figure 1. Schematic diagram of hybridization Cu–CuxO nanoparticles on plasma-treated graphene (PTG) [47].

Apart from combining Cu and graphene, other groups of researchers investigated the performance of three kinds of carbon nanotube (CNTs) including MWCNTs, N-doped MWCNTs, and carboxylated MWCNTs with Cu as a composite paste for power electronic packaging application. Cu particles composed of spherical NPs (20-60 nm), sub-micro-particles (0.2-0.6 μm), and micro-particles (1-2 μm) were mixed with the CNTs dispersion in ethanol. Prior to mixing with Cu, various amounts of CNTs from 0.0 to 1.2 % wt were mixed with anhydrous ethanol with a mass ratio of 100:1 in ultrasound for 1 hour. The pre-sintering process with a temperature of 160 °C was designed to promote the effective removal of organic solvents before proceeding to the actual sintering process at 300 ^{0}C for 100 minutes. The sintered Cu/N-doped MWCNTs produced the smallest resistivity, followed by Cu/carboxylated MWCNTs and Cu/MWCNTs which are 2.252 μΩ·cm, 2.551 μΩ·cm, and 3.571 μΩ·cm, respectively. In addition, 0.6 % wt N-doped multi-walled carbon nanotubes (N-doped MWCNTs) improved the shear strength of pure Cu bonded joint from 23.4 MPa to 23.83 MPa [48].

Based on the studies that had been review, electrical and thermal conductivities, die shear strength and sintering process including temperature and pressure are important parameters in die-attach technology. Excellent electrical conductivity is the main criterion for conductive paste, while high thermal conductivity gives advantages in high semiconductor and high-power electronic applications. Besides, low pressure and low temperature applied in sintered die-attach material gives relative advantages to reduce the production cost, prevent heat stress to electrical component and suitable to any flexible substrate such as polymer, which usually has a low melting point. Notable that silver-based composite material for die-attach or conductive ink is commonly being explored in research and development as it possesses excellent electrical, thermal, and mechanical performances. Yet, the copper-based composite material has become attractive to be investigated recently which offers comparative performance and is more economical than silver material. Thus, the next section will review the advantages and limitations of graphene-based material in composite conductive paste/ink technology.

2.2 Sample Preparation and Sintering Process

Sintering is the process of solid-state material driven by the reduction of total surface energy. During this process, solvent will be decomposed and removed from die-attach and small particles like nano size could give an advantage due to their high surface energy. Non-volatility and little residue of solvent after sintering are the best characteristic of solvent need to be considered. Figure 2 illustrates the bonding mechanism of sintering Ag paste on Cu substrate; before, start and end of the sintering process. A significant number of silver nanoparticles were released from Ag particles at a certain range of temperature which serves to promote the sintering process. In addition, the bonding process between silver particles and Cu substrate was happen during the sintering process. At the end of the sintering process, direct Cu bonding between Ag particles was observed. Furthermore, inkjet printing, screen printing, and stencil printing are some equipment used for applying conductive ink/paste onto the substrate. In addition, the sintering process could be processed by using equipment such as hotplate, furnace, vacuum furnace, hot air reflow system, etc.

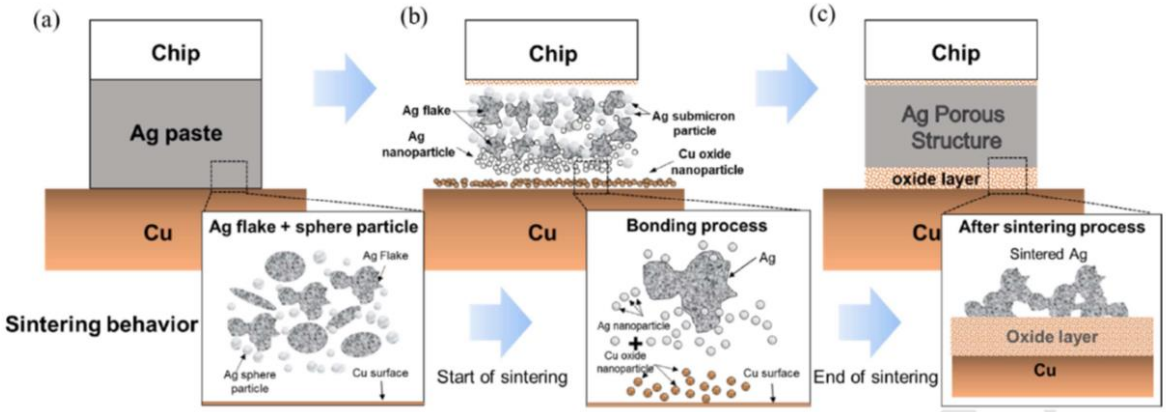

Figure 2. Bonding mechanism illustration of sintering Ag paste on Cu substrate, (a) before sintering; (b) start of sintering; (c) end of sintering [43].

Commonly, the temperature range used for the sintering process starts from 100 ^{0}C to 300 ^{0}C and the condition is applied either in pressure/pressure-less or ambient/vacuum. For example, the temperature of 100 ^{0}C, 150 ^{0}C, 200 ^{0}C, 250 ^{0}C, and 300 ^{0}C were selected in sintering various mixtures of organic solvent e.g., alpha-terpineol, water-free alcohol, and polyethylene glycol 40,000 in the Ag paste for the time range of 10 to 60 minutes in the vacuum drying box. The demonstrated result shows electrical conductivity of silver paste can be improved by increasing the sintering time where 300 ^{0}C for 40 minutes was chosen as an optimum sintering process in the study conducted by [38]. Other than that, sheet resistance of 3.83×10^{-5} Ω.m was measured and nano-silver paste can last long by more than 6 months at room temperature without oxidation and agglomeration phenomenon [38].

Moreover, the sintering process could be conducted in ambient air using the hot plate as presented by [39]. The range of temperature of 200 ^{0}C, 250 ^{0}C, 280 ^{0}C, and 300 ^{0}C under a pressure of 0.4 MPa was set up for sintering Ag paste between two Ag-plated Cu for 30 minutes using a hot plate. The result illustrates that Ag pastes exhibit a high die shear strength of 80 MPa at 280 ^{0}C under a small sintering pressure of 0.4 MPa and 3 μΩ/cm in resistivity. The strength is far higher and resistivity is almost equivalent to that expensive Ag nanoparticle (<20nm) paste [39].

According to another study performed by [43], sintered dummy Cu chip attach was using hybrid Ag paste on bare Cu substrate in ambient condition. The sintering process was observed at a temperature range of 180 to 300 °C for 60 minutes. The excellent property of hybrid paste allowed the paste to sinter at the optimum temperature of 250 °C without assisted pressure in air and reached about 30.0 MPa of shear strength. Cu substrate produced Cu_2O nanoparticles (NPs) when heat was supplied, and its volume matched well with self-generated AgNPs during the sintering process. Thus, the robust bonding strength was performed which mutual bonding formed between two materials that produce a high interfacial strength [43].

Furthermore, a hot air reflow system could be utilized for the sintering procedure as conducted by [44]. Cu to Cu Ag-plated Cu substrate was sandwiched with colloidal silver paste and sintered at 200 °C for 20 minutes. After the sintering process, thermal conductivity was measured as high as 229 W/m·K which was 4.5 times higher than that of Sn-Pb solders (51 W/m·K) [44]. Other than that, [46] used Lenton horizontal tube furnace to sinter the composite of AgCu paste in the open air at 380 ^{0}C for 30 minutes. Disc shape AgCu paste was prepared using a mold-die set and hydraulic press, and sample mold-die was compacted into the green body with 1500 psi (10.34 MPa) of pressure which mimic the actual applied pressure upon the die placement and attachment process on a die-attach material. The thermal conductivity was measured using Nano flash laser system and sintered disc-shape (thickness of 2.0-2.2 mm) was rapidly heated on one side with the surface temperature of 25, 150, and 300 ^{0}C and the temperature rise at another side was measured, finally the best thermal conductivity e.g., 159 W/m K was calculated [46].

Other researcher used a vacuum furnace with 5 MPa of pressure for the sintering process. As a sample preparation, graphene/Cu paste was poured into the cylindrical mold with an inner diameter of 12.7 mm and covered with the cylindrical column with an outer diameter of 12.7 mm before the sintering process. The sample was sintered at 300 ^{0}C for 30 minutes and a thermal diffusivity instrument (NanoFlash) was employed to evaluate the thermal conductivity of the composite sample. The proper amount of graphene acts as the local network which connecting copper particles inside each graphene sheet and improving the heat conduction with the advantage of ultrahigh in-plane thermal conductivity of the graphene (thermal conductivity of copper matrix up to 123.5% compared to oxide-free copper paste) [47]. In summary, the optimal sintering temperature is in the range of 200 ^{0}C to 300 ^{0}C with various sintering times e.g., 20 minutes up to 60 minutes, depending on the properties of the materials used. Low sintering temperature with high die shear strength of die-attach sample gives advantages in die-attach technology, especially in high power applications. Table 1 shows the summary of research conducted by the previous researcher which includes material, material size, solvent, percentage of conductive filler, electrical and thermal performances, and sintering temperature.

3. CHARACTERIZATION OF PASTE

Viscosity, electrical, thermal, and mechanical characterizations are important characterizations involved in the development of conductive ink/paste. This section will focus on the thermal conductivity measurement.

3.1 Thermal Characterization

The thermal conductivity of a material is a measurement of how well or poorly it conducts heat. The theory of thermal conductivity can also be described by the rate at which heat passes through a specified material, expressed as the amount of heat that flows per unit time through a unit area with a temperature gradient of one degree per unit distance. Figure 3 shows an example of sample configuration during thermal conductivity for the sandwiches of Cu-Cu with conductive paste in the middle. Other than that, a dummy chip or chip could be used during the characterization.

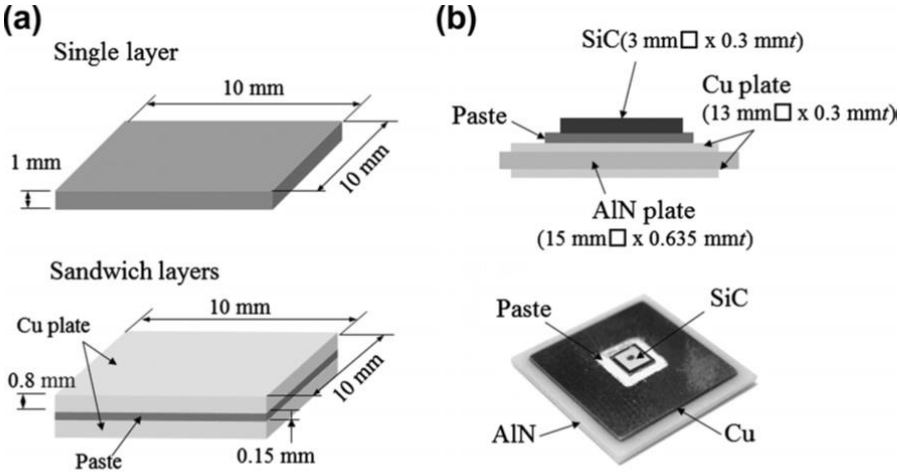

Figure 3. (a) Thermal conductivity measurement samples. Sandwiches of Cu-Cu substrate which the upper and lower were for intrinsic thermal conductivities and the lower is for those with thermal resistivity, respectively. (b) SiC die-attach setup and photograph [34].

According to Wiedemann-Franz Law, the electrical and thermal conductivities of pure metals are related by referring to equation 1 below:

$$\lambda = (L\cdot T)/\rho \qquad (1)$$

where λ is the thermal conductivity (in Watts/m K), T is the absolute temperature (in K), L is the Lorenz Constant (2.45x10-8 $Volt^2/K^2$), and ρ is the electrical resistivity (in Ω•m).

Note that electrical resistivity is the inverse of the conductivity which means the thermal conductivity is directly proportional to the electrical conductivity measurement.

However, in non-metal-like carbon-based material heat is conducted by other methods. For example, compounds of pure carbon have varying degrees of conductivity which could be different depending on the atomic arrangement. The relation between electrical and thermal in pure metal is invalid to apply in carbon compound where notably that diamond has perfect electrical insulator, but its thermal conductivity is greater than that of any metallic materials. Therefore, several types of thermal measurement methods can be applied such as guarded hot plate and transient laser flash methods.

Figure 4 illustrates the experimental setup of the transient guarded hot plate method. The guarded hot-plate (GHP) method measures the heat capacity in the specimen. The proposed test bench provides temperature and heats flux measurements at the material borders for the paralleled piped shaped/circular composite. In between two horizontal aluminum heat exchangers is an ample gap. Thermo-regulated baths, which supply the exchangers, enable a fine temperature management of the injected fluid with the precision of around 0.1 degrees Celsius. On each side of the composite, heat flux sensors and thermocouples (type T) are installed.

The method of preparation is by locating the sample between two horizontal aluminum heat exchangers. The heat flux sensors and thermocouples (type T) are placed on each side of the composite. The whole thing is maintained in place with the use of a slightly tightened pneumatic jack. Various sensors are connected to a Labview program adapted to measure heat flux and temperature fluctuations. Experimental data are recorded with regular and adjustable time steps (6s). The lateral side faces are insulated by polyethylene expanded foam (PE) which reduces the multidimensional heat transfer to a 1Dimension problem [49].

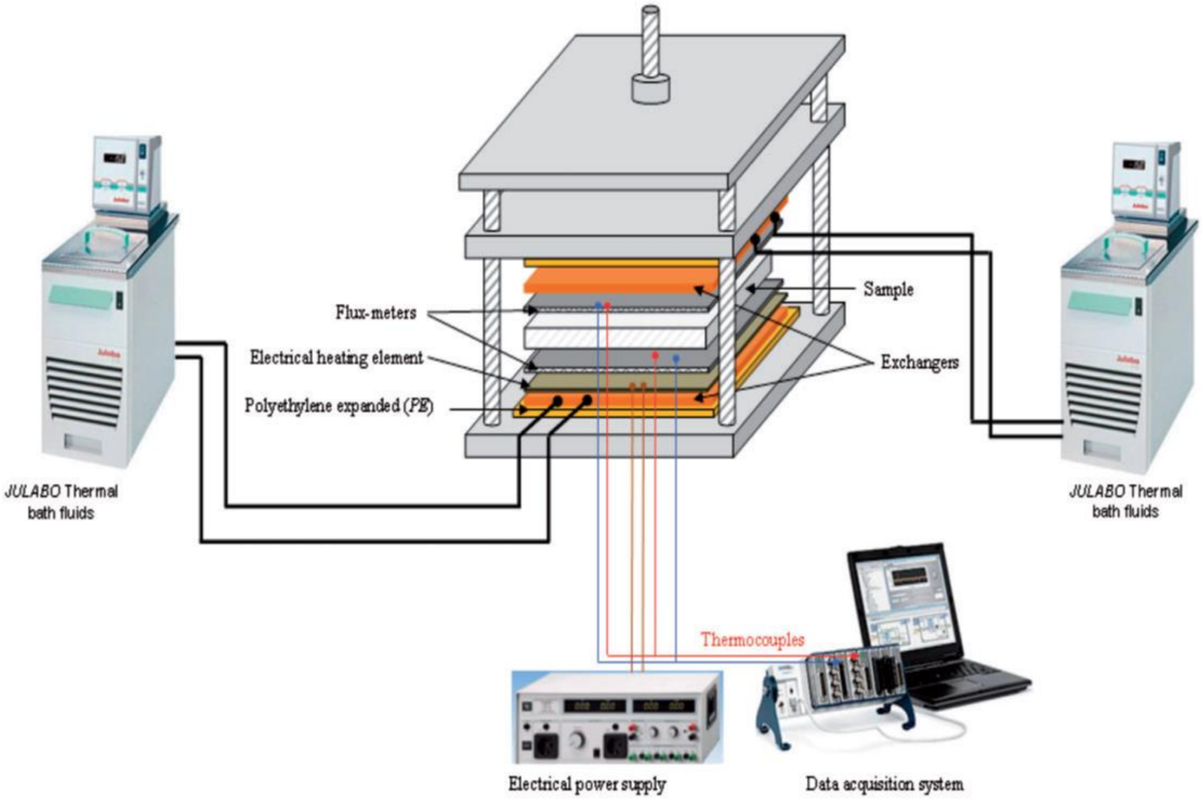

Figure 4. Experimental set-up of transient guarded hot plate method [49].

A material's thermal conductivity is strongly influenced by a variety of factors. These factors include the temperature gradient, material characteristics, and the length of the heat flow. Thermal conductivity could be calculated using Fourier's Law as mentioned in Equation 2.

$$k = \frac{QL}{A(T_2 - T_1)} \tag{2}$$

where,
k = Thermal conductivity
Q = Rate of heat flow (W)
L = Length or thickness of material (m)
A = Surface area of the material (m^2)
T_2-T_1 = Temperature Gradient (K)

Table 1 Summary of Research Including Material, Material Size, Solvent, Percentage of Conductive Filler, Electrical and Thermal Performances, and Sintering Temperature.

Die-Attach/ Conductive Paste	Material Used	Material Size	Solvent	Percentage of Conductive Filler	Resistivity/ Sheet Resistance	Thermal Conductivity	Sintering Temperature
[34]	Ag particles	micron-sized & submicron-sized Ag	ethanol and ethylene glycol	88 %	3.9×10^{-6} Ω	140 W/m K	200 ⁰C
[38]	silver nanoparticles	300 nm	alpha-terpineol, water-free alcohol, and polyethylene glycol 40,000	70 %	3.83×10^{-5} Ω.m	-	300 ⁰C
[39]	micron flakes sub-micron	diameter, d: 8.0 μm, thickness, t: 260 nm d: 0.3 μm	4-(tert-butyl) cyclohexyl acetate as a dilute agent and HPMDA	94 wt%	3 μΩ/cm	-	280 ⁰C
[44]	colloidal silver	13 nm	Disperse in NaNO3	97.5 wt %	-	229 W/m·K	200 °C
[46]	Ag Cu	(40 ± 10 nm) (50 ± 10 nm)	(resin binder) and solvent (terpineol and ethylene glycol)	87 wt %	-	159 W/m K	380 °C
[47]	graphene copper	(1–3 layers, 8–12 μm in length/ ≤100 nm width	n-butanol and terpineol	70 wt %	-	168.5 W/m K	300 ⁰C
[48]	Cu: spherical NPs, sub-micro-particles micro-particles MWCNTs, N-doped MWCNTs carboxylated MWCNTs	20-60 nm 0.2-0.6 μm 1-2 μm	Organic solvent	88 wt%	2.252 μΩ·cm	-	300 ⁰C

4. GRAPHENE IN CONDUCTIVE PASTE/INK AND ITS FUTURE PLANNING

As mentioned before, the combination of graphene and metallic materials illustrates a very promising result as described by [47], which specifically focuses on the thermal interface behavior of graphene and copper nanoparticles. Previously, broads research about graphene has been discovered e.g., exfoliation step to produce graphene, specific solvent for dispersing graphene, and graphene surface treatment, as dispersibility is the main challenge for graphene-based materials. In order to fully utilize the great benefits of graphene, [32] produced high conductivity graphene ink by the exfoliation of graphite in ethanol and ethyl cellulose (EC). Graphene flakes (thickness: ~2 nm and areas of ~50 × 50 nm^2) were produced by the exfoliation of graphite in ethanol via sonication and centrifugation method which was reported in previous work [50]. Graphene/EC dispersed in ethanol with the ratio of~1:100 to remove large graphite flakes. To remove excess EC and solvent, NaCl(aq) was added, and the dispersion was centrifuged to collect graphene/EC solid. The polymeric binder EC encapsulates graphene flakes (2.4 wt % solids) was then mixed with cyclohexanone/terpineol (ratio 85:15, respectively) and printed on low-surface-energy Si/SiO_2 substrate. The sample was annealed for 30 minutes in a range of temperature between 250 °C to 350 °C. The 250 °C annealing temperature shows the lowest in resistivity, where 4 mΩ.cm was measured [32].

[38] synthesized Ag/RGO composite to improve the conductivity of the ink with silver nanoparticles (Ag NPs) and promoted the dispersivity of RGO to avoid nozzle jam. Graphene oxide (GO) was prepared from pristine graphite by the modified Hummers method, polyvinyl pyrrolidone (PVP) was utilized as both reductant and stabilizer and NaOH was added to enhance the reduction of GO. Silver nitrate ($AgNO_3$) aqueous solution was utilized to synthesize the Ag NPs on the RGO sheet, while ethanol and ethylene glycol were used as a solvent to produce conductive ink. The Ag/RGO composite was served as one of the promising conductive ink fillers for printable flexible electronics which Ag NPs were anchoring on the surface of the reduced graphene oxide (RGO) sheet. Electrical conductivity 2.0×10^3S/m was attained with the sheet resistivity of 0.5kΩ/□ (as the thickness was measured to be 1 μm) at the baking temperature of 80 ^{0}C to 100 ^{0}C and the result was comparable with the hybrid graphene/Ag baking in 300 ^{0}C [51]. Thus, a low cost, high conductivity, and good dispersivity of conductive ink for inkjet printing was successfully developed [38].

In-situ chromium (Cr) carbide formation by matrix-alloying of reduced graphene oxide (RGO)/CuCr composites were fabricated by [52]. A flaky copper ((~5 μm) and Cr ((~5 μm) powder were added with GO suspension and annealed at 400 ^{0}C for 3 hours to produce RGO/CuCr composite. The effect of sintering temperature resulted from the formation of Cr carbide on the interface structure of RGO/CuCr composite enhanced the mechanical properties of graphene/CuX composites interface structure like wettability and satisfactory strength-ductility combination. This study focused on the mechanical performance of the sample where the yield strength of 2.5 vol% RGO/CuCr sample improved about 222% (267MPa) as compared to the CuCr sample [53]. Further investigation related to electrical and thermal conductivities is not mentioned in this study, however, it shows the versatility of graphene to hybrid with other metallic materials.

[54] coated graphene layer on bare Cooper (Cu) substrate to improve the thermal and electrical conductivity of direct Ag sinter joining on bare Cu for silicon carbide (SiC) die-attach in high-temperature applications. Single-layer graphene was covered on the Cu substrate by chemical vapor deposition (CVD) as oxidation protection and improvement in mechanical reliability. The thickness of Cu oxide on Cu substrate with graphene layer was significantly smaller than that without graphene and only appeared at the location of Cu grain boundaries which result in sintered Ag contacted with Cu oxide to form a robust interface bonding. Sinter Ag paste was formulated with the mixing of micron-sized flake particles, submicron-scale Ag spheres, and ether-type as a solvent. Sintering temperatures ranging from 180 °C to 350 °C were applied to mount SiC on the Ag paste and sintered on a hotplate [54]. The appearance of Cu oxide such as Cu_2O possessing very poor thermal conductivity of 3.2–5.6 W/mK at high temperature [55].

The Cu oxide thickness on the copper substrate without graphene coating dramatically increases when the sintering temperature increases to 350 °C. Meanwhile, for copper substrate with graphene coating at 350 ^{0}C, the Cu oxide thickness is almost the same as the sinter Ag joining on the bare Cu structure without graphene coating in the case of sintering temperature of 250 °C. This paper discussed useful information of Cu substrate as heat effect in sintering process will change Cu to Cu oxide, for example, Cu_2O in range temperature of 190 ^{0}C to 200 ^{0}C and change to CuO at the temperature of 240 ^{0}C. The appearance of Cu oxide will affect the electrical, thermal, and mechanical performances of die-attach materials.

Recently, research related to graphene-based material are usually discovered in the application of inkjet printing. [56] prepared graphene sheets decorated with silver organic nanoparticles for inkjet printing. Ethyl cellulose, cyclohexanone, and terpineol were mixed with graphene prior to the addition of silver. The fabricated ink needed to be sintered using a hot plate at 300 ^{0}C for 40 minutes. Prior to the mixing, the as-received graphene sheet was heated up from room temperature to 2200 ^{0}C for 30 minutes. After 15 times of printing, resistivity of 4.62 x 10^{-4} Ω m and conductivity of 2.16 x 10^3 S/m were achieved [51]. Another study fabricated Ag/G hybrid conductive ink for writing electric which graphene (diameter of 0.5–2 µm, thickness of 0.8 nm) hybrid Ag and silver nanoparticles with capping agent (ethanol, and ethylene glycol and glycerol) were mixed and the ink was applied using roller ball pen. A typical resistivity value measured was 1.9 x 10^{-7} Ω m after sintering at 100 ^{0}C for 60 minutes [57].

Graphene-based or graphene hybrid paste/ink for inkjet printing application seldom studies about the thermal conductivity as it is not the main concerned parameter. Either graphene or graphene oxide is widely used in the application as both materials have their advantages and limitations. For example, in conductive ink application for inkjet printing, some researchers choose to employ GO due to its cost-effectiveness, massive scalability, versatility for chemical functionalization, and easy processability into paper-like materials, coatings, composites, etc [56]. Besides, some groups tend to choose graphene with specific solvent and high-temperature treatment as dispersibility is the main limitation. Moreover, graphene is a single-layer defect-free material that is costly to produce to a scalable degree [58], highly reactive surface, and difficult to prepare as a solution [11]. However, graphene provides better performance compared to rGO especially in electrical performance [59-60].

While GO is an insulating material that can be obtained in larger quantities by the oxidation of graphite and then continue with exfoliation of graphite oxide during the synthesizing process using Hummer's method [61-62] or modified Hummer's method [63-64]. Potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 35 %), sulfuric acid (H_2SO_4, 98 %), and hydrochloric acid (HCl, 37 %) are the main chemicals that are used in the production of GO [65-67]. Figure 5(a) and (b) illustrate the chemical structure of graphene, GO, and rGO, and synthesizing process of rGO from graphite, respectively. The conductivity of GO can be partially restored after reducing GO to produce rGO [68-69] using reducing agent e.g., hydrazine (N_2H_4), [70-71], sodium borohydride ($NaBH_4$), ascorbic acid ($C_6H_8O_6$), sodium hydrosulphite ($Na_2S_2O_4$) and sodium hydroxide (NaOH) [66].

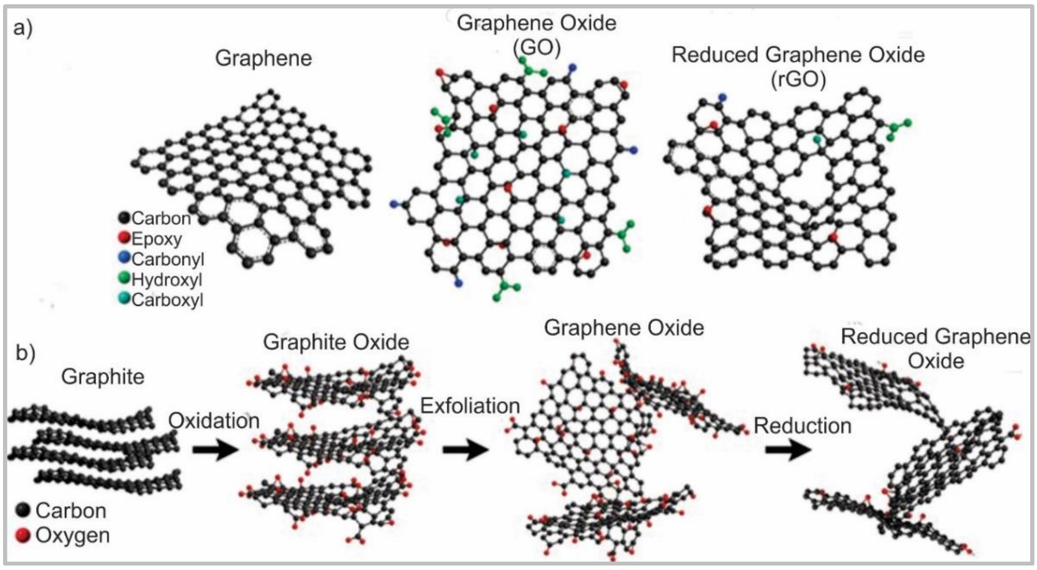

Figure 5. (a) Chemical structure illustration of graphene, graphene oxide, and reduced graphene oxide. (b) The synthesizing steps of reduced graphene oxide from the graphite material [58].

Many researchers had utilized RGO as the main material in conductive ink since it offers several advantages such as inexpensive raw materials, the potential for scalability, low thermal budget, and compatibility with additive printing techniques. However, the electrical conductivity of RGO is inferior to pristine graphene, and defects of GO or RGO are difficult to be repaired perfectly like graphene even after the reduction or sintering processes. This is because repairing the defect requires temperature as high as 1600 °C [73-75]. The defect will cause a phonon scattering effect to occur and reduces the thermal conductivity performance which is not recommended in power electronic die-attach application [52, 76].

However, research conducted by [47], give an opening eye to graphene rather than GO as oxygen plasma treatment could be used for graphene surface treatment to enhance the dispersibility of graphene in solution. The oxygen plasma treatment is easy to control and environmentally friendly. The treatment does not introduce any additives or significantly damaging the graphene-like by adding any surfactant or functionalized it with harsh corrosive acid. Other than improving the dispersibility of graphene, defect of graphene could be repaired easily without applying high degree temperature.

For future planning in die attach material, hybridization silver and treated graphene surface using oxygen plasma is one of the composites that are interesting to be explored. A combination of in-situ silver nanoparticles on graphene surface and the additional function of self-generated silver nanoparticles using silver flake on graphene sheet are expected to improve the die attach performance especially in thermal conductivity and mechanical properties. Reducing silver particle size to the nanoscale is beneficial by taking advantage of high surface energy and low sintering temperature could be achieved. This phenomenon could give advantages in overcoming the reliability issues resulted from the high sintering temperature such as in terms of chip performance and power electronic packaging.

As mentioned before, Wang and co-researcher measured 229 W/m.K of thermal conductivity for colloidal silver paste while [47], show 168.5 W/m.K of thermal conductivity for graphene/Cu which those values are among the highest value in die-attach hybrid metallic materials. Other than that, Cu substrate is commonly employed in electronic industries due to its low cost. However, Cu substrate could be oxidized in ambient and also during the sintering process. The appearance of graphene-based on the die attach composite should be beneficial to both components which are the substrate and die. As the hybrid graphene/copper shows a positive impact in thermal conductivity, hybrid graphene/silver with two different sizes of silver particles have been attracted to be investigated. Thermal conductivity outcomes higher than 250 W/m K of new sintered graphene/silver are expected to be fabricated.

5. CONCLUSION

The development of conductive ink/paste has been significantly explored as the increment of demand in the electronic industry such as a flexible electronic and high semiconductor. Silver becomes widely used in the power electronics industry as it has several advantages like high electrical conductivity and thermal conductivity. However, the cost is still high comparing to copper. Moreover, copper has an equivalent quality to silver material but the oxidation layer on copper gives a crucial challenge in its applications. Hybrid graphene with metallic material has been proposed with the expectation to enhance the performance of metallic paste for example in reducing the oxidation effect of copper and reducing the weight percentage used of silver that can lower the processing cost. Furthermore, excellent material properties of graphene might be utilized to improve the application of hybrid graphene metallic paste for instance in thermal conductivity and die shear strength. The selection of graphene rather than graphene oxide is highly recommended as the defect on graphene is lesser as compared to graphene oxide which affects the performance in graphene-based materials specifically in electrical and thermal conductivity.

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