

Preparation of Silver and Graphene Paste with a Specific Ratio of Organic Solvent

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ABSTRACT

Sintered silver is the most commonly used material used in the die attach technology. Conventional solder materials cannot meet the requirement, especially for high-power electronics due to their low melting temperature. Recently, the development of hybrid sinter conductive paste has become an interesting field to be explored since hybrid sinter paste is expected to provide extraordinary properties as compared to non-hybrid materials. Graphene and silver are two types of hybrid materials that are extensively explored as both materials have superior properties like high electrical and thermal conductivity. This paper focuses on optimizing the formulation of organic solvent; 1-butanol and terpineol with the formation of graphene nanoplatelet (GNP) and silver flake as a paste. The best ratios of 1-butanol to terpineol in formulating the GNP and silver flake were 20:80 and 45:55, respectively. The sheet resistance of silver paste was inversely proportional to the increase of temperature which the sintering process was expected to occur between the silver-silver and silver-copper at 200 °C.

Keyword: Graphene nanoplatelet, silver flake, hybrid sinter paste, thermal conductivity, sintering process

1. INTRODUCTION

The ongoing demand for electronic applications such as flexible electronics, power electronics like the high-speed train, and light-emitting diodes (LED) are adopting the conductive paste in a mass manufacturing environment. This phenomenon attracts extensive research to be conducted in the field of conductive paste fabrication especially in improving thermal conductivity and mechanical performance. Conventionally, soldering is perhaps the most popular method used in the interconnection surface joining technologies (SMT). The solder-reflow process temperature to melt lead-free or high-lead solder paste or solder preform film is in a range of 260 to over 300 °C. The solder alloys unfortunately are reported to have low electrical and thermal conductivity, as well as high sensitivity to fatigue failure under cyclic loading due to low yield strength and increasing of high inelastic strains during deformation. Besides, the low melting temperature of solder attachments in the junction becomes one of the foremost challenges to power modules when the operating temperature is very close to melting temperature or raised to 175 °C or even higher [1].

As an overcome to the low melting temperature of several types of solder alloys, Pb-based solder material has been used for decades in the electronic industry as it can provide the high melting temperature. However, Pb-based material could give harmful effects on human health and the environment. Other than Pb-based solder, others Pb-free solder materials that produce high melting temperature are Au-based [2] and Zn-Al-based [3 - 4]. However, Au-based is extremely high-cost while Zn-Al-paste needs to undergo a complicated process.

As an alternative to the solder method as well as to overcome the limitation of solder materials, high-melting-point metals such as silver and copper are widely used in microelectronic packages and hybrid fabrication. Over those solder performance, silver has superior electrical and thermal conductivity such as $6.3 \times 10^5 (\Omega \text{ cm})^{-1}$ and 429 to 459 W/m K, respectively, which is higher than soldering with 0.6 to $0.9 \times 10^5 (\Omega \text{ cm})^{-1}$ electrical and 50 to 70 W/m K thermal conductivity [1]. Specific sintering temperatures applied during the heating process of metal-based paste could provide optimum performance of the paste. The size of the material can affect the sintering temperature during the process, for example, micrometer-sized Ag in an organic binder needs to be heated over 650 °C to form an acceptable electrical and thermal performance. The sintering temperature of silver paste can be lowered below 300 °C by using a nanoscale of silver materials [5].

[6] attached a 10 mm x 10 mm chip on a copper substrate using a nanoscale of paste with 1 MPa of pressure and drying at 185 °C. Other researchers used silver nanoparticles paste for low-temperature electronic packages when the chip bonding area is large (\geq 100 mm²) and the other researchers fabricated tape casting with a sintering temperature of 300 °C using a hotplate, [7 – 8], respectively. Recently, sintered hybrid nanoparticles conductive paste becomes an opening new technology in the conductive paste industry due to its promising characteristics. The combination of different types of material in the hybrid materials could alter the existing properties of the material, thus inducing extraordinary properties which normally enhanced the properties of pure metal or polymer.

Recently, sintered hybrid conductive pastes of metal-based such as silver-graphene or coppergraphene are widely developed as graphene possesses high thermal conductivity (5300 W/ mK), excellent electronic transport properties, and excellent mechanical stiffness [9]. However, sintered hybrid silver is the most popular material used in the die-attach industry since it can be applied in a harsh environment due to high-melting-point and other excellent properties [10]. [11] prepared hybrid conductive ink composed of Ag nanoparticles and graphene-Ag composite nanosheets and loaded them in commercial rollerball pens as writing electronics devices on paper substrate. While another researcher fabricated inkjet printing ink composes of annealed graphene nanosheets/ Ethyl cellulose (EC) and silver/organic complex as the main component and printed the conductive ink on polyimide (PI) [12].

Previously, many related research on hybrid conductive paste has been conducted, but limited information regarding the formulation of organic solvent or capping agent in the fabrication process of conductive paste was mentioned. This is because each material has a different molecular weight and a high ratio of conductive filler to an organic solvent is expected to give better performance. This paper focuses on the specific ratio of organic solvent with the formulation of graphene nanoplatelet (GNP) and silver flake as a paste. The main organic solvents discussed in this paper are 1-butanol and terpineol, and the performance of the formulated paste is observed in terms of the condition of the product and electrical performance.

2. MATERIALS AND METHOD

Materials used are Graphene Nanoplatelets (GNP) with particle sizes of 5 μ m and 2 5 μ m with a surface area of 120 to150 m²/g, silver flakes (10 μ m, \geq 99.9% trace metals basis) and 1-Butanol 99.9% were received from Merck KGaA, Darmstadt, Germany. Terpineol was purchased from Gouden Sdn Bhd. The sonication process using an ultrasonic bath was employed as a main fabrication process in the whole experiment.

2.1 Preparation of Hybrid Silver (Ag) Powder with Different Concentrations of GNP in Ethanol

GNPs of 0.05wt %, 0.1wt %, and 0.3wt % were prepared in 5 ml of ethanol, respectively, before 0.015 g of silver flakes (SF) were mixed in the solution. Before mixing with SF, the GNP suspension was sonicated in ethanol for 10 minutes and the sonication process was continued for 1 hour just after the SF was added into the solution. The dispersibility performance between GNP in ethanol and SF was observed during the sonication process and the mixed solution was heated on the hotplate under constant stirring (200 rpm) at 40 °C until most of the ethanol evaporated to the environment. The dried solution was cured in the oven for 30 minutes at 250 °C and the dried hybrid material was collected and pounded to become a fine powder.

2.2 Optimization of Organic Solvent in Fabrication Conductive Paste

There are multiple choices of solvent or capping agent that could be used in fabricating a conductive paste and in this experiment, 1-Butanol and terpineol were chosen as a combination of organic solvent in producing a paste [13]. GNP and SF paste were fabricated separately to investigate the optimum ratio between organic solvent to conductive filler due to different molecular weights between GNP and SF of 12.01 g/mol and 107.87 g/mol, respectively. 0.2 g of GNP was measured and mixed with different ratios of 1-Butanol to terpineol using Thinky mixer with the ratio 1-Butanol to terpineol of 10:90, 20:80, 31:69, and 70:30, respectively. The structure of the paste was observed, and the electrical performance of each paste was measured using the four-point probe in terms of resistivity measurement. Based on the optimum organic solvent ratio result gained in the GNP paste, the experiment was continued with the fabrication of SF paste using the previous optimum result as a reference ratio. The organic solvent ratio 1-butanol and terpineol of 20:80, 16:84, and 45:55 were applied in preparing SF paste and, the condition and electrical performance of the paste in terms of resistivity were observed.

3. RESULT AND DISCUSSION

3.1 Fabrication of Hybrid G/Ag

Carbon-based materials like CNT and Graphene have limitations in poor dispersibility. GNP suspension was prepared with different concentrations of GNP in ethanol. Figure 1 illustrates the collected hybrid G/Ag powder after being heated in the oven for 30 minutes at 250 °C. Three different concentrations of GNP of 0.05 wt%, 0.1 wt%, and 0.3 wt% were prepared in the ethanol. Prior to the curing process, the GNP suspension in ethanol was sonicated for 10 minutes and SF with an amount of 0.015 g was immediately added to the suspension, and the sonication continued for 60 minutes. This experiment was mainly focused on the dispersibility of GNP in ethanol as well as the performance of silver flake in the GNP suspension.

Table 1 shows the dispersibility observation of GNP and SF suspension in ethanol after 60 minutes of sonication. From the observation, GNP and SF dispersed in ethanol after 60 minutes of sonication, and few sedimentations appeared after 1 night of preparation. This result shows that GNP can form a relatively stable dispersion in ethanol and is supported by the finding gained

by the previous researcher [14]. However, notable that there are many sediments observed when the suspension was sonicated only for 20 minutes. This experiment was conducted to investigate the performance of GNP in ethanol as a beginning preparation step for preparing hybrid G/Ag paste. To avoid waste in material, the experiment was conducted with a very minimal volume of materials, thus, only hybrid powder from 0.3 wt% of GNP was able to be collected and measured.

| Observation | Before | After |
|-------------|-----------------|-------|
| 0.05 wt % | | |
| 0.01 wt % | 2001s grughp | |

Table 1 Observation of GNP Suspension Before and After 60 Minutes of Sonication

On the other hand, the dispersibility performance of GNP in distilled water had been tested and the comparison images between dispersed in ethanol and distilled water are illustrated in Table 2. From the observation, the 0.05wt % of GNP dispersion in ethanol indicates the GNP dispersed thoroughly in the ethanol after 1 hour, and no changes can be noticed after 4 hours of sonication time. However, the agglomeration of GNP powder and the floating GNP powder at the distilled water surface can be seen after 1 hour and 2 hours of sonication time. Furthermore, after 4 hours of sonication process, most of GNP powder can be observed disperse in distilled water but there was floating GNP powder at the surface of the water. Other than that, the separation layer between distilled water and GNP (sediment) was observed after 1 night left at room temperature.

To avoid waste in material, the experiment was conducted with a very minimal volume of materials, thus, only hybrid powder from 0.3 wt% of GNP was able to be collected and measured as illustrated in Figure 1. About 0.9451 g of hybrid powder was weighed and other samples of 0.05 wt% and 0.1 wt% were difficult to collect and measure. However, this experiment shows positive guidelines in the hybridization of GNP and silver for the purposes of preparing the hybrid conductive paste. Furthermore, this experiment was repeated in the proper amount of material and further investigated in a form of paste especially in terms of electrical and thermal conductivities.

| Table 2 Comparison Images Between GNP Dispersion in Ethanol and GNP in Distilled Water for 1 Ho | ur, 2 |
|---|-------|
| Hours, 3 Hours, And 4 Hours of Sonication Times | |

| Sonication Time | GNP (0.05wt %) in Ethanol | GNP (0.05wt %) in Distilled Water |
|-----------------|---------------------------|--------------------------------------|
| 1 hour | | GNP |
| 2 hours | | |
| 3 hours | | |
| 4 hours | | |



Figure 1. a) Sample 0.3 wt%, b) 0.1 wt% and c) 0.05 wt% of GNP and silver flake after furnace in 250 °C for 60 minutes, and d) collected powder of 0.3 wt% G/Ag after drying process.

3.2 Optimization Ratio of Organic Solvent for GNP Paste and Silver Paste

In this experiment, 1-butanol and terpineol were chosen as an organic solvent of the paste by referring to a study conducted by [13]. At the early stage, the optimization ratio of organic solvent was conducted separately between GNP and silver flake. The main challenge is to adjust the suitable ratio of 1-butanol to terpineol when the amount of GNP or silver was fixed. Table 3 indicates the result of GNP paste form with various organic solvent ratios such as ratio 1-butanol to terpineol of 10:90, 20:80, 31:69, and 70:30. All the mixtures of powder show the paste form, but the ratio of conductive filler is still lower compared to the portion of organic solvent. The performance of each paste was investigated in terms of sample sheet resistance measurement where the sample was prepared on the Cu substrate and cured in the oven at different temperatures of 100 °C, 150 °C, and 200 °C.

In addition, Table 4 illustrates the optimization result of silver flake paste form with various organic solvent ratios of 1-butanol to terpineol with the values of 20:80, 16:84, and 45:55. The adjustment ratio was started with the ratio of 1-butanol to terpineol of 20:80 which this ratio is based on the best ratio of producing the GNP paste. However, the result shows the silver flake paste changed to silver ink and was too liquid. The ratio of 45:55 indicates the best appearance of silver paste and the ratio between conductive filler to organic solvent is higher compared to the other mixtures. The silver paste was applied on Cu substrate and cured at various temperatures to observe the effect of sheet resistance when different temperatures were applied. Figure 2 presents the real image of the silver mixture on the Cu substrate before curing in the oven. It can be observed that, the big separation layer between conductive filler to organic solvent for the ratio of 1-butanol to terpineol; 20:80 followed by 16:84.



Figure 2. The image of silver mixed with organic solvent on the Cu substrate.

Table 3 Results of GNP Paste Form with Various Organic Solvent Ratios of N-Butanol to Terpineol with
The Values of 10:90, 20:80, 31:69 and 70:30

| GNP | N-Butanol (g) | Tripenol (g) | Ratio n-butanol:terpineol | Ratio (Filler:Solvent) | Observation |
|------|------------------|-----------------|------------------------------|---------------------------|-------------|
| 0.2g | 0.18 | 1.62 | 10:90 | 11:89 | Paste form |
| 0.2g | 0.315 | 1.26 | 20:80 | 12:88 | Paste form |
| 0.2 | 0.585 | 1.305 | 31:69 | 10:90 | Paste form |
| 0.2g | 1.20 | 0.52 | 70:30 | 13:87 | Paste form |

Table 4 Results of Silver Flake Paste Form with Various Organic Solvent Ratios of 1-Butanol to Terpineolwith The Values of 20:80, 16:84, and 45:55.

| Silver Flake | N-butanol (g) | Tripenol (g) | Ratio n-butanol:terpineol | Ratio (Filler:solvent) | Observation |
|-----------------|------------------|-----------------|------------------------------|---------------------------|---|
| 0.2g | 0.1575g | 0.63g | 20:80 | 21:79 | Silver ink was too liquid |
| 0.2g | 0.0264 | 0.1416 | 16:84 | 56:44 | In the form of ink but a bit thicker |
| 0.2g | 0.0264 | 0.0317 | 45:55 | 79:21 | Paste form |

3.3 Electrical Characterization

Figure 3 and Table 5 show the sheet resistance measurement of the GNP paste with different formulations of organic solvent of 20:80, 10:90, 31:69, and 70:30 ratio of 1-butanol to terpineol. The presenting data indicates that GNP with a ratio of 20:80 1-butanol to terpineol shows the lowest in sheet resistance and follows by ratios of 10:90, 70:30, and 31:69 which are 6.71 Ω /sq, 8.49 Ω /sq, 14.39 Ω /sq, and 15.62 Ω /sq, respectively. From these measurements, GNP paste with a ratio of 20:80 1-butanol to terpineol was selected as a reference in preparing SF paste. Since the molecular weight difference between GNP and SF is big where GNP is lighter than SF, thus, a big amount of GNP is equal to a very small amount of SF. Therefore, the amount of organic solvent can affect the produced paste as well as the ratio between conductive filler to organic solvent.

| Table 5 Sheet Resistance of Different Formulations of Organic Solvent in Preparing GNP Paste with The |
|---|
| Curing Temperature of 100°C |



Figure 3. Sheet resistance measurement of different formulations of GNP paste.

Furthermore, Figure 4 and Table 6 show the sheet resistance of the GNP pastes with the formulation of organic solvent 20:80 when compared with the silver paste (45:55) at different curing temperatures of 100 °C, 150 °C, and 200 °C. The results show the sheet resistance of GNP increases when the temperature is increased. However, the sheet resistance of silver paste is inversely proportional to the increase of curing temperature. Terpineol used in this project has a boiling temperature of 219 °C, which could be decomposed when the curing temperature is near to its boiling temperature, such as at 200 °C. This phenomenon affects the structure/physical of the paste after the curing process. For instance, the GNP surface can be observed to be smooth at 100 °C, however, as the temperature increases the appearance of crack can be detected on the dried GNP paste. Besides, the dried GNP paste becomes brittle and easy to detach from the substrate. This is because the organic solvent which acts as a capping agent between GNP particles is decomposed and resulted in the particle being apart from each other, thus, increasing the sheet resistance measurement.

| | Sheet Resistance, Ω/sq | | |
|------------------------|--|---|--|
| Curing Temperature, °C | GNP Conductive Paste (Solvent Ratio, 20:80) | Ag Conductive Paste (Solvent Ratio, 45:55) | |
| 100 | 4.0067 | 1.91x10 ⁻³ | |
| 150 | 4.2700 | 1.49 x10 ⁻³ | |
| 200 | 8.2050 | 0.41 x10 ⁻³ | |

Table 6 Sheet Resistance Comparison Between GNP and Silver Paste at Curing Temperature of 100 °C,150 °C and 200 °C

On other hand, the silver sheet resistance decreases when the temperature increases even when the organic solvent is already decomposed to the environment. This is might due to the sintering process that occurred between silver particles and Cu substrate before their melting point. The dried silver paste surface on Cu substrate can be observed and the dried paste has a smooth surface, no crack, and adhered firmly on the Cu substrate. The sintering does not happen between GNP and Cu substrate since higher temperatures are required to be applied.

Summary of the GNP and silver paste at curing temperature of 100 °C can be referred to in Figure 5. It can be observed that the silver paste has lower sheet resistance which might be due to the higher ratio of conductive filler to organic solvent as compared to GNP paste. In addition, [15] in their research found that silver nanoparticles could be self-generated from the micrometer flake shape of silver particles during the sintering process. Silver nanoparticles are expected to provide higher die shear strength compared to the micrometer spherical shape of Ag particles [15]. In addition, previous research discovered that the single layer of sintered hybrid Ag paste on a soda-lime glass sheet shows high thermal conductivity at the sintering temperature of 200 °C [16].



Figure 4. Sheet resistance measurement of GNP and silver paste with different curing temperatures.



Figure 5. Summary of the GNP and silver paste at curing temperature of 100 °C in 30 minutes.

Then, the experiment is proceeded to formulate the conductive paste with the ratio of conductive filler to solvent of 70:30 and to fabricate the hybrid G/Ag paste which is expected to produce high thermal conductivity.

4. CONCLUSION

The dispersibility of the graphene-based is the main constrain in the formulation of graphene with other materials. GNP can be dispersed in ethanol and mixed with silver flake under the ultrasonication process. The molecular weight of the GNP is lighter compared to silver which same weight of GNP and silver will result in a big amount of GNP powder used. The sheet resistance of silver pastes is lower than GNP paste and the conductive filler ratio to organic solvent of silver is higher than that GNP paste. The optimization result gained from this work can be used as a reference in producing hybrid silver-graphene paste in the future. The information obtained from this work can be used in reducing the wastage of material used in the future work of fabrication and formulation of conductive paste.

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