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Carbon black dispersions and carbon–silver combinations as thermal pastes that surpass commercial silver and ceramic pastes in providing high thermal contact conductance

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Abstract

Carbon black dispersions are superior to the best commercial silver and ceramic particle thermal pastes for providing high thermal contact conductance across mating surfaces that are smooth (0.05 μm). For mating surfaces that are rough (15 μm), the combined use of carbon black and silver is more effective than carbon, silver or ceramic pastes. The use of a silver paste to even out the rough surfaces prior to using the carbon black dispersion is more effective than the use of a carbon–silver mixture. For both smooth and rough surfaces, the carbon–silver mixture is superior to silver pastes. The highest conductance attained for rough surfaces is lower than that attained for smooth surfaces.

Keywords: A. Carbon black, Carbon composites; D. Thermal diffusivity, Thermal conductivity

1. Introduction

Heat dissipation is the most critical problem in microelectronics, as it limits the reliability, performance, power and further miniaturization. Heat sinks are widely used for heat dissipation. They are materials of high thermal conductivity, such as copper. However, effective use of a heat sink requires good thermal contact of the heat sink with the heat source (e.g., the microprocessor of a computer). The mating surfaces are never perfectly flat. There are hills and valleys in the surface topography, thus resulting in air pockets at the interface. Since air is a thermal insulator, it is important to displace the air by using a thermal interface material that conforms to the topography of the mating surfaces. Therefore, conformability is an essential attribute of a thermal interface material.

For any interface material, the thicker it is, the more the thermal resistance that it gives. Thus, a small thickness (ideally just enough to fill the valleys at the interface) is also important for a thermal interface material. For a thermal interface material in the form of a paste (known as a thermal paste), a small thickness can be attained if the paste is highly spreadable. Hence, spreadability is the second criterion.

Thermal conductivity has long been assumed in the industry to be the key criterion, but it is actually less important than conformability or spreadability. As long as the thermal interface material is more thermally conductive than air, its presence can improve the thermal contact. On the other hand, if the thermal interface material is relatively large in thickness, its thermal conductivity will be more important.

Commercial thermal pastes involve thermally conductive particles such as silver and ceramics (e.g., aluminum oxide, boron nitride and zinc oxide). [1] The particle size typically ranges from 0.1 to 10 μm. In contrast, the current authors used carbon black [1]

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[1] http://www.arcticsilver.com.

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which is in the form of porous agglomerates. Within each agglomerate, the particles are of size 30 nm [1], which is smaller than the particles used in commercial thermal pastes. Due to its porous agglomerate structure, carbon black is highly compressible. In contrast, the particles used in commercial thermal pastes are not compressible. The compressibility and the small particle size make carbon black an exceptionally effective ingredient for thermal pastes [1].

Carbon black dispersions based on polyethylene glycol (PEG) or di(ethylene glycol)butyl ether, along with dissolved ethyl cellulose, provide thermal pastes that are superior to solder as thermal interface materials [1]. The thermal contact conductance of the interface between copper discs reaches 3×10^5 W/m^2 °C, compared to 2×10^5 W/m^2 °C for tin–lead–antimony solder. The pastes based on PEG are superior to those based on butyl ether in their thermal stability above 100 °C [1]. Carbon black is superior to materials that are more conductive thermally (graphite, diamond and nickel particles, 0.1 μm diameter carbon filament and single-walled carbon nanotube) in providing thermal pastes of high performance [1,2].

Due to the low degree of roughness of the mating surfaces [1,2], the thermal paste must be able to conform to the submicron undulations of the mating surfaces. For surfaces encountered in practical applications, such as the surfaces of heat sinks and microprocessors, the roughness is typically much more than the submicron level. The need for the thermal paste to fill deep valleys in the surface topography would make the thermal conductivity within the paste more important than when the valleys are shallow. Therefore, the relative performance of a carbon black dispersion (attractive in its conformability and spreadability) and silver paste (attractive in its thermal conductivity) may be different for rough mating surfaces versus smooth mating surfaces. This paper is partly aimed at investigating this possible difference.

This paper also compares the performance of the carbon black dispersions with that of commercial thermal pastes that are recognized by the industry to be the best, [2] namely the products of Arctic Silver Inc. (Visalia, CA). Specifically, these products are (i) Ceramique (density 2.7–2.8 g/ml; oils with aluminum oxide, boron nitride and zinc oxide submicron particles, but without metal particles), (ii) Arctic Silver 5 (density 4.05–4.15 g/ml; oils with over 88 wt.% silver particles, together with a small percentage of submicron zinc oxide, aluminum oxide and boron nitride particles), and (iii) Arctic Silver 3 (density 3.3–3.5 g/ml; oils with over 75 wt.% silver particles, together with a small percentage of micron sized boron nitride particles to improve the flow characteristics). [1]

For rough mating surfaces, the combined use of carbon black and silver may be superior to carbon black alone or silver alone, since carbon black provides the conformability while silver provides the thermal conductivity. Indeed, this synergism is suggested by the observed superiority of a thermal paste made by mixing a carbon black dispersion (provided by these authors) and commercial silver paste (Arctic Silver 3), compared to the carbon black dispersion or to the commercial silver paste. [2] The study in Footnote 2 was made by comparing the temperature rise of a microprocessor connected to a heat sink for various types of thermal paste at the interface between microprocessor and heat sink; the thermal contact conductance was not measured. The mating surfaces in this study are much rougher than those used in the thermal contact conductance measurement in [1,2]. Therefore we here investigate the synergistic use of carbon black and silver for thermal pastes.

This work includes mating surfaces that are both rougher than and the same as those in [1,2]. The synergistic use of carbon black and silver is expected to be not as attractive for the case of smooth mating surfaces, since a high thermal conductivity is not required for a thermal paste that functions by filling shallow valleys only. Nevertheless, this work includes performance data for both smooth and rough mating surfaces for comparison. The smooth surfaces were obtained by mechanical polishing using 0.05 μm alumina particles; the rough surfaces were obtained by mechanical polishing using 600 grit SiC sand paper (with 15 μm SiC particles).

The synergistic use of carbon black and silver can be attained by mixing the carbon black dispersion and silver paste to form a uniform silver–carbon paste, as in Footnote 2. It can also be attained by using the silver paste to fill the deep valleys of the relatively rough mating surfaces (i.e., evening out), followed by applying a thin overlay of carbon black dispersion. The latter method of synergistic use has not been previously investigated, although it is expected to be more effective than the former method. This work compares both methods.

The synergistic use of carbon black and silver is probably akin to that of boron nitride (in a low proportion) and silver (75 wt.%) in a commercial silver paste (Arctic Silver 3) used in this work. The ease of shear of the micron size boron nitride particles may enhance the conformability of the paste. However, boron nitride particles are not compressible like carbon black (hence not as conformable as carbon black) and they are much larger than the carbon black particles (30 nm for the carbon black in [1] and in this work). Smaller particles are preferred due to the need to fill small valleys

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[2] http://www.lostcircuits.com/advice/carbon_black/.

in the surface topography. In addition, boron nitride is more expensive than carbon black.

2. Experimental methods

The formulation, ingredients, preparation method and testing method of the carbon black dispersions of this work are identical to those in our prior work [1]. The carbon black was Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It was a powder with particle size 30 nm, a nitrogen specific surface area 254 m^2/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm^3. The carbon black powder was mixed with a vehicle by hand stirring to form a uniform paste. The particle size (30 nm) of the carbon black is much less than those of the metal or ceramic particles used in the commercial pastes.

Unless stated otherwise, polyethylene glycol (PEG, or $HO(CH_2CH_2O)_nH$) was used as the organic vehicle. We used PEG 400 from EM Science (Gibbstown, NJ). It had an average molecular weight of 400 amu; this average value corresponds to $n \sim 8.68$. It was a liquid at room temperature and contained ethyl cellulose (E8003, Sigma Chemical Co., St. Louis, MO) at 3 vol%. The ethyl cellulose was a white powder that was dissolved in the vehicle and served to improve the dispersion and suspension of the solids in the pastes.

The other organic vehicle used was di(ethylene glycol)butyl ether (from Aldrich Chemical Co., Inc., Milwaukee, WI). It contained ethyl cellulose at 40 vol%, from Sigma Chemical Co.

The pastes were prepared by first dissolving ethyl cellulose in the vehicle (either PEG or butyl ether). Dissolution was performed at room temperature for butyl ether, but at about 60 °C (with heat provided by a hot plate) for PEG. In the case of PEG heating was hastened the dissolution of ethyl cellulose. After this, the thermally conductive solid ingredient was added. Mixing was conducted by using a ball mill and stainless steel balls for 30 min. After mixing, the paste was placed in a vacuum chamber (which involved a mechanical vacuum pump), without heating, for the purpose of air bubble removal.

Various thermal pastes were sandwiched between the flat surfaces of two copper discs (both surfaces of each disc having been mechanically polished by using 0.05 μm alumina particles in the case of smooth mating surfaces and 15 μm silicon carbide particles in the case of rough mating surfaces), which had a diameter of 12.6 mm and a thickness of 1.16 mm for one disc and 1.10 mm for the other disc.

The silver pastes are very viscous compared to the highly fluid nature of the carbon black dispersions. The ceramic paste (Ceramique) is even more viscous than the silver pastes. Therefore, the application of a silver or ceramic paste on a copper disc required manual rubbing of the paste on the surface. Such rubbing was not needed for the carbon black dispersion or the carbon–silver mixture mentioned below.

In this work, a silver–carbon paste was obtained by manual mixing of the carbon black dispersion and Arctic Silver 3 in the volume ratio of 1:2. Mixing of the carbon black dispersion and Arctic Silver 5 produced a paste that was not uniform and not workable, regardless of the proportion used. Therefore, silver–carbon pastes made from Arctic Silver 5 were not evaluated.

In the alternate method of synergistic use of carbon black and silver, silver paste (either Arctic Silver 3 or Arctic Silver 5) was first applied on a rough copper disc by rubbing, followed by manual removal of the excess amount above the copper surface. Then, the carbon black dispersion was applied on the copper surface. Thus, this synergistic use of carbon black and silver involved two layers instead of a mixture layer. For comparison, this paper also addresses such synergistic use of carbon black and ceramic (Ceramique).

The thermal contact conductance between two copper discs with and without a thermal interface material was measured using the transient laser flash method [3–6]. The pressure on the sandwich was controlled at 0.46, 0.69 and 0.92 MPa. This is because pressure affects the thermal contact conductance, even for a material that is not resilient [4]. The thickness of the thermal interface material was 25 μm or less. The uniform distribution of the paste in the plane of the sandwich was made possible by the fluidity of the paste and the use of pressure. The interface material thickness was obtained by subtracting the thicknesses of the two copper discs from the thickness of the sandwich, such that all thicknesses were measured using a micrometer. The interface material thickness for all cases was the same before and after the conductance measurement.

A Coherent General Everpulse Model 11 Nd glass laser with a pulse duration of 0.4 ms, a wavelength of 1.06 μm and a pulse energy up to 15 J was used for impulse heating. The laser power was adjusted to allow the temperature rise of the specimen to be between 0.5 and 1.0 °C. Details of the set-up for thermal diffusivity testing using the laser flash method can be found in [1]. Calibration using a standard NBS 8426 graphite disc (thickness = 2.62 mm) was performed before testing each specimen in order to ensure measurement accuracy. The data acquisition rate used for each test was adjusted so that there were at least 100 temperature data points during the temperature rise.

The experimental error in transient thermal contact conductance measurement consists of random error due to experimental data scatter, and systematic error mainly due to the lag of the thermocouple response and partly due to the method used to calculate the conductance from the temperature data. The higher the thermal contact conductance, the greater the error. The thermal diffusivity of a standard NBS 8426 graphite disk, which had a similar transient temperature rise time as the copper sandwich with the highest thermal contact conductance, was measured prior to testing each specimen in order to determine the systematic error, if any. The random error shown by the ± value was determined from measurement for at least three specimens.

3. Results and discussion

Table 1 gives the thermal contact conductance values obtained for various combinations of thermal paste, mating surface smoothness and contact pressure. For the case of smooth mating surfaces, the conductance is highest for the carbon black dispersion and lowest for Arctic Silver 3. Arctic Silver 5 is superior to Arctic Silver 3, but inferior to the carbon–silver mixture. Ceramique is even better than the carbon–silver mixture, but is inferior to carbon.

For the case of rough mating surfaces, the conductance is highest for the carbon–silver bilayer involving Arctic Silver 5. The superiority of the carbon–silver bilayer involving Arctic Silver 5 to that involving Arctic Silver 3 is consistent with the superiority of Arctic Silver 5 to Arctic Silver 3. Both bilayers are more effective than the carbon–silver mixture, which is in turn more effective than Ceramique, Arctic Silver 3 or Arctic Silver 5. The carbon–ceramic bilayer is superior to Ceramique and to the carbon–silver mixture, but is inferior to both types of carbon–silver bilayer. For the case of rough mating surfaces, carbon is the worst, but synergistic use of carbon and silver results in the best performance.

The highest conductance attained for rough mating surfaces by using a carbon–silver bilayer (Arctic Silver 5) is lower than that attained for smooth surfaces by using carbon. Therefore, the use of smooth mating surfaces is recommended.

The conductance increases with increasing contact pressure for Ceramique and carbon–silver mixture, whether the mating surfaces are smooth or rough. The pressure dependence is less for carbon, Arctic Silver 3 or Arctic Silver 5. In particular, for carbon, the conductance has negligible pressure dependence for smooth surfaces, but increases slightly with increasing pressure for rough surfaces. This behavior of carbon is probably due to the increase of the carbon black volume fraction as the pressure increases and the consequent increase in thermal conductivity of the thermal paste; the thermal conductivity within the paste is more important for rough surfaces than for smooth surfaces.

The value for Ceramique in Table 1 is close to the value $>20\times10^4$ W/m^2 °C reported by the manufacturer. [1] However, the value for Arctic Silver 5 in Table 1 is lower than the reported value of $>35\times10^4$ W/m^2 °C. [1] The method used for thermal conductance measurement and its accuracy have not been revealed by the manufacturer.

The use of solder (63Sn–36.65Pb–0.35Sb, applied in the molten state) in place of a thermal paste as a thermal interface material gave a thermal contact conductance of $(20.08\pm0.60)\times10^4$ W/m^2 °C [2]. No pressure was applied during testing. The thermal contact conductance values reported in this paper for pastes and solder as thermal interface materials were all obtained using the same specimen configuration, testing method and data analysis algorithm. Therefore, the values are reliable on

Table 1
Thermal contact conductance for various combinations of thermal paste, mating surface smoothness and contact pressure

Thermal paste	Mating surface smoothness	Conductance (10^4 W/m^2 °C)		
		0.46 MPa	0.69 MPa	0.92 MPa
Carbon[a,b]	Smooth	29.90 ± 0.79	28.98 ± 2.11	29.63 ± 1.92
Carbon[b,c]	Smooth	27.43 ± 2.75	28.41 ± 2.12	28.03 ± 1.57
Arctic Silver 3[a]	Smooth	13.05 ± 0.90	11.65 ± 1.02	10.82 ± 0.73
Arctic Silver 5[a]	Smooth	17.72 ± 0.23	16.78 ± 0.32	17.29 ± 0.86
Ceramique[a]	Smooth	21.48 ± 1.12	24.10 ± 0.76	25.59 ± 0.96
Carbon–silver[d] mixture[a]	Smooth	17.86 ± 1.43	21.54 ± 2.36	23.30 ± 3.00
Carbon[a]	Rough	4.85 ± 0.13	5.17 ± 0.04	5.28 ± 0.22
Arctic Silver 3[a]	Rough	6.15 ± 0.65	6.80 ± 0.50	6.22 ± 0.26
Arctic Silver 5[a]	Rough	9.79 ± 1.01	10.21 ± 0.69	8.63 ± 0.37
Ceramique[a]	Rough	7.21 ± 0.10	8.47 ± 0.53	9.92 ± 0.41
Carbon–silver[d]mixture[a]	Rough	11.45 ± 0.82	12.89 ± 1.03	14.35 ± 1.00
Carbon–silver[d]bilayer[a]	Rough	17.06 ± 0.44	17.22 ± 0.79	19.61 ± 0.83
Carbon–silver[e] bilayer[a]	Rough	21.18 ± 1.64	20.39 ± 1.39	23.08 ± 1.24
Carbon–Ceramique bilayer[a]	Rough	11.62 ± 0.78	14.19 ± 1.44	17.06 ± 0.46

[a] PEG as vehicle, with 3 vol% ethyl cellulose and 1.25 vol% carbon black.

[b] Data from Ref. [1].

[c] Di(ethylene glycol)butyl ether as vehicle, with 40 vol% ethyl cellulose and 0.20 vol% carbon black.

[d] Arctic Silver 3.

[e] Arctic Silver 5.

a relative scale. The carbon black dispersions and Ceramique (Table 1) are superior to solder, but Arctic Silver 3 and Arctic Silver 5 are inferior to solder.

The superiority of the carbon black dispersions to the commercial silver and ceramic pastes is attributed to the conformability of carbon black. That Ceramique is superior to Arctic Silver 3 or Arctic Silver 5 is probably due to the better conformability of Ceramique. The superiority of the carbon black dispersions to solder is attributed to the conformability of carbon black and to the products of the reaction between solder and copper, as explained in our earlier publication [1].

4. Conclusions

Carbon black dispersions as thermal interface materials are superior to the best commercial thermal pastes (including silver and ceramic pastes) and to solder. In addition to their superior thermal performance, the carbon black dispersions are advantageous in their low cost.

The synergistic use of carbon black and silver is attractive for thermal contacts involving rough mating surfaces, but not for smooth mating surfaces. A carbon black dispersion is the most effective thermal paste for smooth mating surfaces. For both smooth and rough surfaces, the carbon–silver mixture is better than silver pastes. The carbon–silver bilayer is even better than the carbon–silver mixture when the surfaces are rough, due to the filling of the valleys in the topography by silver, which is more thermally conductive than carbon. The highest conductance attained for rough surfaces by using a carbon–silver bilayer is lower than that attained for smooth surfaces by using only carbon.

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