Abstract

Thermal interface materials (TIM) used to improve the conductivity between mating components in an electronic assembly are discussed. A variety of materials including adhesives, gels, greases, fluids were used in this study. Both greases and pastes are considered, to improve the contact resistance of stress decoupling and stress coupling interfaces, respectively. Nanoparticles, micro particles, low melting point (LMP) fillers, and mixtures of nano-micro particles were combined to obtain both decreased interparticle thermal resistance and decreased bulk thermal resistance in thermal pastes. An evaluation of thermal grease filler materials was also conducted. A steady-state conductivity test was employed to measure conductivity. Thermal impedances of materials were measured at various fixed bondline thicknesses ranging from 170 to 53 mm^2 K/W. The performance of greases varied from 70 to 11 mm^2 K/W at low bondline with a varied load. For thermal pastes, cross section measurements were used to measure particle dispersion throughout the interface. The paper also presents a nanoparticle dispersion approach to prepare temperature and time stable nanogels. Several nanogels were evaluated after three years post-preparation, using transmission electron microscopy (TEM), to check particle distribution in the nanogel.

Introduction

High power density electronic packages require efficient heat transfer characteristics to remove thermal energy from the package. Contacting surfaces often make up a significant part of the thermal resistance pathway. Many components in electronics packaging are created at high volume such that near ideal mating surfaces are difficult to achieve. Because non-ideal or engineering surfaces form contacting bumps or asperities, the remaining surface area must be filled with a higher conductivity material than air to achieve efficient heat transfer [1-2].

Thermal interface materials are important materials in electronics packaging intended to fill these gaps between mating surfaces, thus enabling efficient heat transfer [1-16]. The materials commonly fill the space between the die and lid of a package (TIM1) and the lid and heatsink (TIM2). Another application of TIM is between the lid and the substrate (sometimes referred to as TIM3.) [Figure 1] This interface can be less crucial, but it can aid heat flow to a PWB in many applications. The TIM3 material must often possess good adhesive properties in addition to low thermal resistance. One such TIM3 consists of a polymer material to provide adhesion & processing characteristics and filler particles to improve thermal conductivity. Although several TIM are available, the authors believe that existing materials require more improvement so low processing temperatures, flexible and cost effective materials can be developed for large scale production. An effort in this direction is presented in the paper.

Much effort has gone into design of TIM technology in industry; from pastes and greases to gels and phase change materials these materials are often highly specialized for each application [2, 5]. Many authors have attempted to utilize the high conductivity of carbon nanotubes (CNTs) for TIM applications. J. Xu et al. [3] studied the usage of vertically aligned carbon nanotubes (VACNTs) grown by PECVD to increase the conductivity of TIM materials. When combined with a phase change material they were able to realize thermal impedances as low as 5.2 mm^2 K/W. Many other novel techniques have also been employed for TIM development. Kesong Hu. et al. [12] was able to repurpose a type of flexible exfoliated graphite formerly used for gasketing and sealing applications as a highly conductive TIM by impregnating the material with carbon black paste. B. Carlberg, et al. [13] reinforced a highly conductive Indium/Bismuth/Tin alloy with polymer fibers to improve mechanical characteristics for TIM applications. V. Chilasatia et al. [6] studied the use of printed silver nanoparticle inks directly onto die hot spots.

Silver nanoparticles are also commonly used to lower the electrical conductivity of materials. These can sometimes be used in electrically conductive adhesive (ECA) applications. Because electrical and thermal properties of many metals are closely related (by the Wiedemann-Franz law) ECA materials are also interesting from a thermal perspective. H. Jiang et al. [3] proposed a material where the electrical resistivity of a conductive adhesive filled with silver flakes was measured as low as 5e-6 ohm*cm.

Figure 1: Schematic of an assembled module on a PWB.
Materials:
The following three material formulations represent various combinations of thermal interface materials (TIM) used for die attachments. Nanoparticles are used to make thermal paste, gel and grease. The major challenge in the development of nanoparticle based TIM is that incompatibility exists between the particles and polymer matrix, which can lead to particle agglomeration. As a result inhomogeneous materials with poor thermal performance could be obtained. We have used surface treatment process that results in excellent dispersability of the nanoparticles and good quality thermal interface materials.

Adhesives were dispensed between two ¾”x¾” square copper plugs, then cured at 160C for 1hr. Tensile strength was measured at a pulling rate of 0.025 inch per minute, and was measured up to 1778 psi or until the joint ruptured. All adhesives show high tensile strength and showed cohesive failure. However, the micro and nano-micro filled adhesive samples did not show any failure up to 1778 psi, the limit of the testing apparatus. This represents a strength advantage for these materials, which the authors plan on exploring in detail in future work.

A test vehicle was used to evaluate the material formulations with respect to assembly. This TV provides the ability to generate combinations of thermal interface materials suitable higher thermal performance.

Results and Discussions
A variety of composite materials were fabricated, ranging from nanogels to nanofluids. Figure 3 shows nanogels and liquid like materials. Nanogels have higher viscosity, for very low flow characteristics, whereas liquid-like nanofluid materials started flowing within 5 seconds of dispense. Nanogels and liquid-like materials include 5 nm particles dispersed in a polymer matrix, with a fractional range of 5-25% nanoparticles by weight. This provides a nearly molecular level of mixing, which contributes to the nanogels and liquid like materials being very stable. There was no observable separation or precipitation of nanoparticles even after 100 times dilution. All the prepared samples were re-tested after 3 years, and it was found that the nanoparticles remained embedded into polymer matrix. The materials were also heat-treated to 60C, after which there was no observable separation or precipitation from dilute solutions. These observations indicate the mixture
did not sinter with time or temperature, which is essential requirement for good thermal interface material.

**Figure 4** shows TEM images of the nanogel materials after three years of storage, post-preparation. Low resolution TEM images exhibited a random distribution of well-defined particulates, with sizes in the range of 5 to 15 nm. The nanoparticles remained as an individual particle and did not interdiffuse or agglomerate with each other. High resolution TEM images indicated presence of lattice and Moire fringes. Fourier transform data and the lattice and Moire fringes clearly indicate crystalline particles present in the nanogel.

![Figure 4](image)

**Figure 4**: (A-B) TEM image of nanogels, and (C) High resolution TEM images of nanoparticles. Inset: Fourier Transform TEM image.

**Figure 5** shows nano grease samples with graphite and carbon nanotubes. Carbon nanotubes are high surface area materials and require proper treatment to make nanogrease materials. **Figure 6** shows water based nanofluids. Around 1-2% nano particles are dispersed into the fluid.

![Figure 5](image)

**Figure 5**: Photographs of graphite based and carbon nanotube based grease.
Adhesives were prepared by mixing appropriate amounts of the thermally conducting filler powders and polymer solution to form a paste-like material. For thermal conductivity measurements, a thin film of this paste like materials was deposited between two metal plates, pressed to thickness using wire spacers to obtain a fixed bondline, and cured at different temperatures ranging from 150 °C to 160 °C. Figure 7 shows a cross section of cured adhesives.

Materials tested include a commercial silicone adhesive, a silver micro TIM, a silver nano micro TIM, and a nano-micro silver LMP material. These materials were tested at various bondline thickness, with a compressive load of 10lbf. The results for adhesive materials are displayed in Figure 8.

For these adhesives, thermal impedance decreased with decreasing bondline thickness, as expected. The silver nano-micro system was found to have the lowest impedance at higher bondline thickness. At lower bondline thickness (0.05mm), micro particle based adhesive shows lowest value. Low melting point (LMP) filler shows higher impedance at high bondline thickness. However proper, curing of LMP paste at low bondline thickness can reduce impedance as low as 50-60mm² W/K.

Nano-micro particle based systems at higher bondline thickness produce better particle packing which results lower impedance. This implies that the nano-micro material should perform well where a large bondline and/or uncertain surface alignment are required. Note that while the bulk impedance of silver nano-micro TIM is very low, the impedance at low bondline is still high as compare to micro particle based TIM. This is a consequence of interparticle thermal resistance between the silver nanoparticles that have not fully been sintered. Because silver nanoparticles are small, the number of interparticle thermal resistances can be higher than that of a micro particle based TIM.

Figure 8: Adhesive TIM Performance. Thermal impedance as a function of bond-line thickness.

Figure 9. Thermal greases were also tested, with results displayed in Filler particles included Aluminum Nitride, Alumina, Boron Nitride, and Graphite. In this study, silicone greases were highly loaded with various filler materials, such that the addition of more filler did not adversely effect the bondline thickness. The materials were tested between the conducting copper surfaces with various applied compressive loadings from 10 to 40psi at 10psi increments. The materials were also tested at high load (90-100psi), and for carbon filler thermal impedances of as low as 11mm² W/K were observed.
Figure 9: Grease TIM Performance. Thermal impedance as a function of compressive pressure loading.

We experimented with a variety of thermal greases and loading. The filler loading was varied from system to system, to allow appropriate loads for bondline thicknesses of interest. For example, alumina required the highest filler loading whereas carbon nanotube had the lowest loading. In other words, different filler loading could adjust the effective viscosity of grease. Figure 9 shows how the impedance decreased with increasing pressure. Boron nitride shows maximum change. Boron nitride was a highly agglomerated system and a higher loading might be required to breakup the agglomerates, to achieve lower bondline and resulting thermal impedance. Thermal greases display significantly improved results when compared to adhesives at the lower bondline thicknesses as shown in figure 9. This is due to the fact that despite their typically lower bulk conductivity, they are both less viscous and they can adapt to relative thermal motion after assembly. This makes the materials better at conforming to non uniform areas between the asperities of the contacting surfaces. These materials will perform better where good alignment can be achieved.

Module Assembly:
A few optimized TIM were used for lid attachment schemes on module assemblies. Customized thermally conductive joints were formed using a curing process. The paper also describes a multiple paste dispense approach to provide efficient heat dissipation; several electrically conductive pastes were tested in a thin bond line construction as thermal interface materials. Here we highlight recent developments two paste systems. As a case study, an example of nano-micro paste or grease and commercially available silicone as thermal interface material for a flip-chip plastic ball grid array package with a 150 μm die pad pitch is given. The paste or grease is dispensed in the middle of the die. A second structural adhesive is a thermally conductive silicone. The thermal silicone is dispensed on the corners of the die. The combination of these two adhesives was dispensed in sufficient volume to achieve greater than 90% area coverage over the die.

Figure 10 shows variety of dispenses patterns for single or multiple adhesives. Figure 10 A-B shows conductive adhesives dispensed in the middle, and thermally conducting adhesives dispensed at the corners. Alternatively, in Fig 10C, it is also possible to use commercial adhesive in the middle and a second adhesive at the corner.
Conclusions

Adhesives, gels, greases, fluids were used as thermal interface materials (TIM). Nano-micro material based adhesives showed the lowest thermal impedance and highest mechanical strength among all tested adhesives. Nanogels and nanogreases maintained their particle distribution with time and temperature exposure. Graphite based grease had lowest impedance among all the materials tested. A few optimized TIM configurations of more than one material were used for lid attachment, for efficient heat dissipation. By designing a appropriate composite materials with these advanced fillers, one can obtain an overall solution to develop next generation packaging with efficient cooling systems.

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References