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Exceptionally high thermal conductivity of thermal grease: Synergistic effects of graphene and alumina

Wei Yu [a], Huaqing Xie [a, *], Luqiao Yin [b], Junchang Zhao [c], Ligang Xia [c], Lifei Chen [a]

[a] *College of Engineering, School of Environmental and Materials Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China*
[b] *School of Mechatronic Engineering and Automation, Shanghai University, Shanghai 200444, China*
[c] *Shanghai Yueda New Materials Science and Technology Ltd., Shanghai 201209, China*

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ABSTRACT

A remarkable synergistic effect between graphene sheets and alumina particles in improving the thermal conductive properties of the novel thermal grease is demonstrated. The use of hybrid size alumina filler leads to compact packing structure in the silicone base and hinders the aggregation of graphene to form clusters. The two-dimensional graphene with superb thermal conductivity can bridge the alumina particles to form more compact packing structure and provide faster and more effective pathways for phonon transport in thermal grease. These synergistic effects decrease the thermal boundary resistance and enhance the thermal conductivity of the thermal grease. The addition of graphene is only 1 wt.%, and the maximum thermal conductivity of the novel thermal grease is 3.45 W/m K. It is significantly improved compared with the thermal grease without graphene (2.70 ± 0.10 W/m K). With respect to the silicone base, an enhancement in thermal conductivity of 2553% is obtained. Meanwhile, a correction theoretical model is proposed by modifying Burggeman asymmetric model, and the model predictions are in reasonable agreement with the experimental values.

1. Introduction

Recently, with the miniaturization and increasing power of electronic devices, the dissipation power density increases rapidly in these downscaled devices. The heat dissipation has become one of the most critical problems that limit the performance, power, reliability and further miniaturization of electronic devices [1–3]. It is well-known that the reliability of devices is exponentially dependant on the operating temperature of the junction, whereby a small difference in operating temperatures can result in a two times reduction in the lifespan of a device [4]. Therefore the heat generated from the devices should be removed as quickly and effectively as possible to maintain the temperatures of the devices at a desired level. Traditionally, heat sinks are used to dissipate the heat from the devices. However, the performance of a heat sink to dissipate heat is sharply limited due to interfacial thermal resistance arising from the mismatch of non-surface flatness and surface roughness of both the devices and the heat sink [5,6].

For the sake of reduction of interfacial thermal resistance, suitable thermal interface materials (TIMs) are utilized to bond the contact surfaces of heat sink and devices [7]. An ideal TIMs possessing high thermal conductivity and strong deformability must conform to the surface topography of the mating surfaces and can take the place of air and fill in the gaps at the interface [8–10]. Because the thermal conductivity of TIMs is much higher than the replaced air (which is only 0.026 W/m K), the interfacial thermal resistance is reduced giving rise to low temperature of the electronic component junction [2]. Currently, thermal interface materials can be classified as thermal greases, elastomeric thermal pads, solders and phase change materials [7,10,11], among which thermal greases, a type of thixotropic pastes with high thermal conductivity, can fill the gaps of the mating surface more effectively. Thermal greases are generally made of two primary components i.e. a polymer base and ceramic fillers. Silicone is commonly used as the base for its good thermal stability, wetting characteristics and low modulus of elasticity [12,13]. Ceramic fillers [13–16] such as alumina, aluminum nitride, boron nitride, silicon carbide, which are highly thermally conductive but electrically insulative, have been used in this system.

Graphene is a two-dimensional nanocarbon material with the hexagonal packed structure compromised of sp^2-hybridized carbon

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* Corresponding author. Tel./fax: +86 21 50217331.
E-mail address: hqxie@sspu.edu.cn (H. Xie).

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atoms. Graphene and its derivatives have attracted intensive interest in many fields due to their exceptional physical and chemical properties [17–19], such as high electrical conductivity [20], superb thermal conductivity [21] and high mechanical strength [22,23], etc. The superb thermal conduction property of graphene discovered by Balandin et al. [21], revealed the thermal conductivity values in the range from 2000 W/mK to 5200 W/m K near room temperature. This discovery has opened a new window for graphene's applications in thermal management fields. Yu et al. [24] explored the graphite nanoplatelet (GNP)-epoxy composite thermal interface materials and attributed the outstanding thermal properties of TIMs to a favorable combination of the large aspect ratio, two-dimensional geometry, stiffness, and low thermal interface resistance of the GNPs. Shahil et al. [25] synthesized polymer composites filled with graphene and multilayer graphene. It could lead to an extremely strong enhancement of the cross-plane thermal conductivity of the composites. The modeling results suggested that these TIMs outperform those with carbon nanotubes or metal nanoparticles owing to graphene's large aspect ratio and low Kapitza resistance at the graphene–matrix interface. The thermal conductivity of graphene prepared by different methods differs greatly. Yu et al. [26] reported silicone thermal greases based on graphene prepared by different procedures, that an enhancement of thermal conductivity was obtained. Theoretical model analyzing validated that graphene is an effective thermally conducting filler to let grease have high thermal conductivity with low filler content. Goli et al. [27] fabricated graphene-enhanced hybrid phase change materials for thermal management of Li-ion batteries, which showed record-high thermal conductivity enhancement. Based on the rapid growth of interest in the thermal properties of graphene, Balandin [28] reviewed the thermal properties of carbon materials focusing on recent results for graphene, carbon nanotubes and nanostructured carbon materials with different degrees of disorder. He also described the prospects of applications of graphene for thermal management of electronics.

The idea of using hybrid fillers containing two or more traditional fillers has already been explored in some literature. It has been demonstrated that the improvements of composite performances can be achieved by combining the advantages of each filler [29,30]. For example, the complex systems of boron nitride and multi-walled carbon nanotube [31], graphite nanoplatelet and carbon nanotube [32], alumina and zinc oxide [6], graphene and silver particle [33] have been used for improving the thermal conductivity of thermal interface materials. Up to now, study on the thermal conductive silicone grease reinforced with hybrid filler consisted of graphene and alumina as we know it has not been reported. Generally speaking, TIMs are electrical insulating materials to prevent short circuit of electronic devices. Novel thermal grease with high thermal conductivity and electric insulation is developed by addition of graphene and alumina in this study. Due to the synergistic effects of graphene sheets and alumina particles, a significant thermal conductivity enhancement is observed.

2. Experimental

2.1. Materials and sample preparation

The α-Al_2O_3 with a purity of 99.5% and average particle sizes of 0.7 and 5 μm were used as received from Nippon Steel Materials Co., Ltd., Japan. The silicone oil and flake graphite were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China and used directly without further purification. The other reagents were analytical grade and also purchased from Sinopharm Chemical Reagent Co., Ltd.

The graphite oxide was prepared by the improved Hummers' method [34], and then the graphene was obtained by the exfoliation of graphite oxide through thermal shock on rapid exposure to temperatures of 800 °C in nitrogen for 30 s [35].

The novel thermal greases were prepared as follows: the hybrid size alumina particles with different weight ratio were mixed in the appropriate weights with the silicone base by using a lab high-speed disperser (SFS-S, Shanghai SIEHE Mechanical Electrical Equipment Co., Ltd., China) at a speed of 3000 rpm for 30 min, then quantitative graphene was added to the mixture and dispersed at a speed of 5000 rpm for another 30 min. For comparison, the thermal grease only filled with alumina particles was prepared by the same procedure.

2.2. Characterization

SEM images were taken on a field-emission scanning electron microscope (S4800, Hitachi, Japan). TEM images were obtained by using a transmission electron microscopy (2100F, JEOL, Japan). The thermal conductivity of samples was measured with a thermal conductivity analyzer (C-Therm TCi, C-Therm Technologies Ltd., Canada), which is based upon a modified transient plane source method. This method is non-destructive and convenient for thermal conductivity measurement of materials in the states of solid, liquid, powder, and mixed. The TCi system consists of a sensor, power control device, and computer software. A spiral-type heating source is located at the center of the sensor, and heat is generated at the center. The heat that has been generated enters the material through the sensor during which a voltage decrease occurs rapidly at the heating source, and the thermal conductivity is calculated through the voltage decrease data. The testing capabilities of the system is 0–100 W/m K across a wide range of temperature (−50 to 200 °C) and the accuracy of the instrument is better than 5%. For this measurement, the samples were filled into the mould with a thickness of 2 mm and kept at 25 °C. The electrical insulation properties of the thermal greases were characterized by withstanding voltage tester (ZHZ4C, Shanghai Anbiao Electronics Co., Ltd., China) according to the ASTM D149 standard.

3. Results and discussion

3.1. Morphology of samples

The size and the shape of fillers have an effect on thermal conductivity of composite. The size and the shape of different Al_2O_3 particles were observed by scanning electron microscope, as shown in Fig 1. The Al_2O_3 particles are almost spherical with average particle sizes of 5 (Fig. 1a) and 0.7 μm (Fig. 1b), respectively. As seen from the SEM image in Fig. 1c, a fluffy and crumpled morphology of graphene is viewed, which also demonstrates thin and wrinkled platelets transparent to electrons. Transmission electron microscopy was also used to examine the exfoliated graphene sheets, as shown in Fig. 1d. The graphene sheet has wrinkles and folded regions with a lateral size of micrometers.

3.2. Thermal conductive properties of thermal greases

The filler size distribution has a great influence on thermal conductivity of composites [36]. Cumberland and Crawford [37] have calculated the maximum packing volume fraction of binary mixture of spheres as a function of composition with diameter ratios as a parameter. According to their results, the packing volume fraction increases with the increase of volume fraction of small particle to reach a maximum value, while decreases with further increase. Fig. 2 shows the thermal conductivity of thermal grease as