



# Magnetically-functionalized self-aligning graphene fillers for high-efficiency thermal management applications



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## ABSTRACT

We report on heat conduction properties of thermal interface materials with *self-aligning* “magnetic graphene” fillers. Graphene enhanced nano-composites were synthesized by an inexpensive and scalable technique based on liquid-phase exfoliation. Functionalization of graphene and few-layer-graphene flakes with Fe<sub>3</sub>O<sub>4</sub> nanoparticles allowed us to align the fillers in an external magnetic field during dispersion of the thermal paste to the connecting surfaces. The filler alignment results in a strong increase of the apparent thermal conductivity and thermal diffusivity through the layer of nano-composite inserted between two metallic surfaces. The self-aligning “magnetic graphene” fillers improve heat conduction in composites with both curing and non-curing matrix materials. The thermal conductivity enhancement with the oriented fillers is a factor of two larger than that with the random fillers even at the low ~1 wt.% of graphene loading. The real-life testing with computer chips demonstrated the temperature rise decrease by as much as 10 °C with use of the non-curing thermal interface material with ~1 wt.% of the oriented fillers. Our proof-of-concept experiments suggest that the thermal interface materials with functionalized graphene and few-layer-graphene fillers, which can be oriented during the composite application to the surfaces, can lead to a new method of thermal management of advanced electronics.

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## 1. Introduction

The increasing power densities in electronics made efficient heat removal a crucial issue for progress in information, communication and energy storage technologies [1–6]. Development of the next generations of integrated circuits (ICs) and ultra-fast high-power transistors depend on efficient heat removal [3,4]. High-power-density devices such as Gallium Nitride (GaN) field-effect transistors (FETs) and GaN light-emitting diodes used in solid-state lighting require a better thermal management technology than is currently available [7–9]. Decreasing the temperature rise,  $\Delta T$ , in GaN transistors by only 10 °C doubles the life-time of the device while decreasing  $\Delta T$  by 20 °C increases the transistor mean-time to failure by an order-of-magnitude [7]. A comparable reduction in the operating temperature of silicon (Si) complementary metal-oxide-semiconductor (CMOS) transistors would allow the chip manufacturers to substantially increase the clock speed of ICs. The demands for better thermal management are not limited to electronics.

The power generation technologies for the photovoltaic solar cells also require efficient thermal management. Modern solar cells have an efficiency of ~15% in the conversion of light to electricity [10–12]. More than 70% of solar energy is lost as heat and has to be removed from the cell to prevent performance degradation [12–14].

The most important and commonly used component of passive thermal management is thermal interface material (TIM). There are different types of TIMs, including curing and non-curing thermal pastes, phase-change materials and solid heat spreaders. The function of TIM is to fill the voids and grooves created by the imperfect surface finish of two connecting surfaces and to improve surface contact and the conduction pathway across the interface. Typical TIM consists of a base (matrix) material and fillers, which are used to increase the overall thermal conductivity. Conventional fillers include silver, aluminum oxide and other metal or ceramic particles. Large loading fractions ( $f > 50$  vol.%) may be required in order to achieve desirable thermal conductivity. Development of more efficient TIMs is crucial for improving heat removal and reducing  $\Delta T$  of a wide range of devices. The common strategy for improving TIM performance is finding the right filler material with high intrinsic thermal conductivity, which can couple well with the matrix and attach to the connecting surfaces. While the thermal conductivity and thermal resistance of TIM are important characteristics of the material, the ultimate metric for the performance of TIMs is the

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temperature rise reduction, which can be achieved within a given device – heat sink assembly.

The discovery of unique heat conduction properties of graphene [15–18] promptly led to the proposals of the use of graphene and few-layer graphene (FLG) as fillers in TIMs [19–23]. In the thermal context, we consider a flake to be FLG rather than a piece of graphite as long as its thickness is below 7–10 atomic planes, and correspondingly, Raman spectrum is different from that of bulk graphite [24]. For practical thermal applications, FLG can have certain benefits as compared to single layer graphene. The thermal conductivity of FLG is still high and it is subject to less degradation when FLG flake is embedded inside matrix material as compared to that of graphene [18]. The larger cross-sectional area of FLG translates to higher heat fluxes along the length of the flake as compared to single-layer graphene. Significant enhancement of the bulk thermal conductivity of epoxy with the addition of a proper mixture of graphene and FLG (with the loading  $f < 10$  vol.%) was reported in several studies [19–23]. The results with other matrix materials such as paraffin wax ( $C_nH_{2n+2}$  hydrocarbons) were also promising [25,26]. The above mentioned studies used randomized but uniform mixture of graphene and FLG fillers in the matrix. A uniform dispersion of the fillers and the absence of air bubbles are important for the improved heat conduction properties of the prepared composites [21–23,26,27].

The theory considerations for graphene composites [28,29] and experimental results for other types of fillers suggest that a strong increase in thermal conductivity at small loading fraction  $f$  can be achieved if the fillers are aligned along the direction of heat flux. In the TIM context the direction of alignment should be perpendicular to the connecting surfaces, thus, facilitating heat transfer from one surface (e.g. computer chip) to another (e.g. heat sink or package). Recent molecular dynamics (MD) simulations predicted that one can achieve a tremendous  $\times 400$  enhancement of the thermal conductivity along the direction of the graphene flake alignment at small  $f = 5$  vol.% in common matrix materials [28]. In the direction perpendicular to the alignment no thermal conductivity increase was obtained. The experimental results with other fillers, such as carbon nanotubes (CNTs) [30–37], are in line with this theoretical prediction. TIMs with low graphene and FLG filler loading ( $f < 5$  vol.%) are strongly preferable because high  $f$  results in increased viscosity, air gap formation and agglomeration, which degrade heat conduction properties. The low loading of graphene is also beneficial for keeping the price of TIMs within an acceptable range.

In this paper, we show that functionalizing graphene and FLG with  $Fe_3O_4$  nanoparticles can help one to achieve the goal of alignment of the fillers during the dispersion of the TIM. The proposed method is inexpensive and scalable for industrial use. The strongly enhanced heat conduction properties are evidenced from the measurements of the *apparent* thermal conductivity and temperature rise in actual heat generating devices. The testing with computer chips demonstrated that the temperature rise can decrease by as much as 10 °C with use of non-curing thermal interface material with  $\sim 1$  wt.% of the oriented graphene fillers. Previous experiments with aligned fillers used CNTs grown by the chemical vapor deposition (CVD) or by the microwave plasma-enhanced chemical vapor deposition (PECVD) [30–37]. The approach based on CVD growth requires high temperature processing and complicated assembly. It is also prohibitively expensive for most TIM applications. Our results indicate that TIMs with low loading of functionalized graphene and FLG fillers, which can be oriented during the composite application to the surfaces, have the potential for a breakthrough in thermal management of advanced electronics.

## 2. Synthesis of the graphene-enhanced thermal interface materials

The graphene and FLG solution was produced following the scalable liquid-phase exfoliation (LPE) method [38,39]. The functionalization was achieved via the recipe previously developed for CNTs used in magnetic and biomedical applications [40,41]. It involves poly-sodium-4-

styrene-sulfonate (PSS) as a wrapping polymer and polyelectrolyte poly-dimethyl-diallylammonium chloride (PDDA) for a homogeneous distribution of positive charges [42–49]. In this approach, the positive charges ensure the adsorption of negatively charged magnetic nanoparticles onto the surface of graphene and FLG by means of electrostatic interactions. The process produced graphene fillers dressed with magnetic nanoparticles of  $\sim 10$  nm average diameter. We also found that a mixture of graphene and FLG flakes with magnetic nanoparticles followed by temperature treatment under certain conditions likewise resulted in attachment of nanoparticles to graphene fillers without these intermediate chemical processing steps.

The functionalization of graphene with magnetic nanoparticles followed the CNT route, which was demonstrated for applications other than thermal management [40–51]. The method combines polymer wrapping technique (PWT) and layer-by-layer (LBL) self-assembly allowing the non-covalent attachment of nanoparticles to the carbon filler leaving intact their structure and thermal properties (see Fig. 1). The non-covalent bonding is an important aspect of the procedure because it preserves the intrinsically high thermal conductivity of graphene [18,27]. Stronger covalent bonding sometimes used for increasing CNT filler – matrix coupling often results in defect formation leading to phonon scattering and TC reduction at least at some filler loading fractions [27]. We utilized poly-sodium-4-styrene-sulfonate (PSS) as a wrapping polymer providing stable dispersions of carbon fillers (both CNTs and graphene). Owing to the high density of sulfonate groups on the negatively charged polyelectrolyte PSS, the PSS coating acts as a primer on the graphene surface for subsequent homogeneous adsorption of the cationic polyelectrolyte poly-dimethyl-diallylammonium chloride (PDDA) through the electrostatic interactions [41,52,53]. The deposited PDDA layer, in its turn, provides a homogeneous distribution of positive charges. The positive charges ensure the efficient adsorption of negatively charged magnetic nanoparticles onto the surface of graphene by means of electrostatic interactions. The adsorption of nanoparticles (diameter range  $D \sim 6$ –10 nm) on graphene surfaces is achieved more effectively than that on CNT surfaces due to CNT's high curvature, which hinders the formation of dense coatings. The magnetic nanoparticles prepared in solution (basic pH) are negatively charged and therefore are electrostatically attracted to the positively charged PDDA layer adsorbed on graphene fillers. It was reported for CNTs that the pH for the most efficient adsorption of  $Fe_3O_4$ – $\gamma$ - $Fe_2O_3$  nanoparticles on polyelectrolyte was found to be 11.9–12.0 [41].

The steps for preparing epoxy-based TIMs with “magnetic graphene” fillers were similar to the ones described by some of us elsewhere for regular LPE graphene [19] (see Fig. 2). The epoxy based components were weighed with the intended loading wt% of LPE graphene powder to the resin (Epoxy-Mount Resin 145–10,010) and the hardener (Epoxy-Mount Hardener 145–10,015) at the manufacturer's 10:3 ratio guideline. The composites were evenly mixed (Flacktek DAC 150) under vacuum conditions. The vacuum pump accessory was used to evacuate the bubbles trapped as a result of mixing dry materials with liquids. The optimized speed mixer setting was found to be approximately 500 rpm for 20 s. The low mixing speed and time were used owing to the high shearing of the dry graphene powder in the non-cured epoxy at higher mixing speeds ( $> 1000$  rpm) that caused the epoxy to cure faster than desired. Several cycles of mixing and vacuuming were applied to achieve the uniformly mixed composites. The composites were then exposed to a magnetic field ( $H = 1.2$  T) for flake ordering. The synthesis of non-curing TIMs with “magnetic graphene” followed a similar process. We used commercial base (Loctite TCP 4000 D PSX-D). The base material was weighted and the desired graphene loading fraction was added using a speed mixer (Flacktek DAC 150) for uniform distribution. The mixing was performed from 300 rpm to 1000 rpm for 1 min to 5 min between incremental additions of graphene filler to the base material until the desired weight percent of graphene, viscosity and smoothness were achieved. The process was carried out under vacuum conditions to evacuate air bubbles

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