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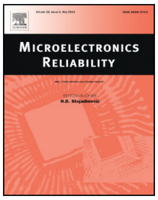

Preparation and thermal properties of the graphene–polyolefin adhesive composites: Application in thermal interface materials

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ABSTRACT

Graphene mixed with epoxy for thermal interface material (TIM) has been well researched. However, some issues emerge when epoxy is used as matrix material, such as overflow problem, non-uniform thickness, needing solidification time, etc. In order to avoid the above issues, a new high performance phase change material (PCM) is prepared by incorporating graphene with polyolefin hot melt pressure sensitive adhesive (HMPSA). The thermal conductivity and hardness of graphene/HMPSA (GHMPSA) composites are both measured and found to be increased with the increase of filled graphene. Due to the increasing hardness, the smallest thermal contact resistance is achieved with 6 wt.% graphene, not 10 wt.%, even the biggest thermal conductivity of GHMPSA is 5.6 W/(mK) with 10 wt.% graphene. The comparison between the present GHMPSA TIM and other commercial TIMs indicates that the present GHMPSA composite is a commendable TIM in reducing thermal contact resistance.

1. Introduction

Rapidly increasing integration level in electric devices brings not only promotions in the property of chips, but also issues in removing the huge heat flux generated from the chips. One of these issues is that the existence of thermal contact resistance (TCR) in electronic packaging results in high temperature step between two contact surfaces under high heat flux, which leads to the high temperature of chips accordingly. Such issue significantly depresses the reliability of microelectronic components and becomes a key challenge in thermal management with the continuous development of chips' power density. Thus, thermal interface material (TIM) was proposed and investigated to reduce TCR and improve the reliability of electronic chips.

So far, most of TIMs are manufactured by compositing polymer or grease with high thermal conductive materials. The matrix materials determine the types of TIMs, such as thermal greases, thermal conductive adhesives, phase change materials (PCMs), thermal pads, thermal gels, etc. [1,2]. And the high thermal conductive materials are applied to upgrade the total thermal conductivity of TIMs. Traditional TIMs, because of the small thermal conductivity of polymer or grease, often require a filling volume of high thermal conductive materials (such as Cu, Al or AlN) as large as 50% to achieve the thermal conductivity of TIMs up to 1–5 W/(mK) at room temperature [3], which limits the development of TIMs. For example, although thermal greases and thermal conductive adhesives have the problems of overflow, controlling thickness, curing, etc. [2], most investigations and applications are still focused on them because their low viscosity can accommodate large filling volume which highly promotes the total thermal conductivity. For comparison, those kinds of TIMs that can be easily handled, such as phase change materials, thermal pads, etc., are seldom employed due to their low thermal conductivity caused by their high viscosity which is not suitable to incorporate in a filler with high fraction. However, the recent discovery of graphene which has an extremely high intrinsic thermal conductivity ($k \approx 5300$ W/(mK)) has broken this limit [4–8], even a small filling volume of graphene can also perform a huge promotion in the thermal conductivity of composites. Yu et al. [9] mixed graphene with silicone thermal greases, a thermal conductivity enhancement of 668% was obtained with a graphene loading of 4.25 vol.%. Yu et al. [10] incorporated graphene with epoxy resin, the thermal conductivity of the composite material can be up to 6.45 W/(mK) when the filling volume of graphene is 25%. Veca et al. [11] prepared a composite with stripping graphene and epoxy resin, when the filling volume of graphene was 33%, the in-plane thermal conductivity of the composite reached 80 W/(mK). Shahil and Balandin [12] used multilayer graphene as filler, the experimental results showed that, when the filler volume $f = 10\%$, the thermal conductivity of graphene/epoxy composite was 5.1 W/(mK) which had an enhancement of 2300% compared with ordinary epoxy resin. In addition to adding graphene alone, incorporating graphene with other high thermal conductive materials as fillers can also have a big enhancement on the thermal conductivity of composites. Yu et al. [13] mixed single-walled carbon nanotubes and graphene with epoxy resin, the thermal conductivity of the composite was 3.35 W/(mK)

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when the mass fraction of the filler was 10%–20% and the ratio of single wall carbon nanotubes to graphene was 1:3. Goyal and Balandin [14] applied graphene and silver nanoparticles as filler, the results indicated that an enhancement of nearly 500% appeared in thermal conductivities when the temperature was changed from 300 K to 400 K with 5% filler volume. Kim et al. [15] prepared the modified $Al(OH)_3$-coated GO composite, the thermal conductivity of 3 wt.% GO/epoxy composite was nearly twice that of the neat epoxy. All these researches revealed that graphene is an excellent filler in developing TIMs, and the huge promotion of composites' thermal conductivity brought about by a small filling volume of graphene is able to accelerate the development of TIMs, especially for PCMs [16], thermal pads, etc.

Therefore, in order to guarantee the reliability of microelectronic components and bring convenience to the processes of electronic packaging, we would like to investigate a high performance TIM that contains the following features: high thermal conductivity, ability to conform to profiles of mating surfaces, do not need curing, can be easily handled, and do not have the delamination issues and thermal stress problem caused by various CTEs. To realize these features, graphene and the polyolefin hot melt pressure sensitive adhesive (HMPSA) are applied to investigate a new PCM in this paper. Different from the thermal conductive adhesives formed by the commonly used matrix material epoxy in most of the literature [10–15], the PCM manufactured by HMPSA is able to be used without curing process, thus it is much easier to handle. Moreover, at normal temperature, the PCM is similar to thermal conductive adhesives, which can adhere to the surfaces of heat sink or chip directly without overflow problem. And when the chip's working temperature is increased, the PCM is able to transform from solid state into liquid phase, which can effectively fill gaps at interfaces, conform to the surface profiles, and reduce the TCR [16–20]. As for the disadvantage of PCMs, which is the low thermal conductivity, filling graphene will be an excellent method to upgrade the total thermal conductivity of the composites. While the high viscosity of matrix materials in the PCM means that it cannot have high filler fraction, the thermal phase change materials are too hard to be used at the interface. Therefore, in this paper, the influences of graphene weight percentage on thermal conductivity, hardness, and thermal contact resistances are all measured and analyzed to discover an appropriate graphene filling fraction for graphene/HMPSA (GHMPSA) TIM, which is able to have high thermal conductivity, appropriate hardness, and a big reduction of TCR. Meanwhile, the present GHMPSA TIM is also compared with other commercial TIMs regarding its properties.

2. Experimental methods

2.1. Preparation of the GHMPSA composites

The graphene used in this paper is prepared by direct liquid-phase exfoliation method from Nanjing SCF Nanotech Ltd, the actual layer number of graphene is smaller than 10, illustrated in Fig. 1(a) and (b). Due to the van der Waals force between adjacent graphene layers, it is difficult to disperse graphene in polymers, organic solvents, or water, and its interface compatibility with other media is poor. Therefore, surface modification is highly necessary for graphene to obtain superior performance in composites.

One commonly used surface modification of graphene is acidification [21,22], which is usually applied with epoxy to result in the esterification reaction. Although HMPSA does not have oxygenic functional groups, acidification is also able to elevate the compatibility between graphene and HMPSA to a certain degree.

To prepare acidified graphene, graphene is first added to a certain volume of concentrated sulfuric acid with 4 h magnetic stirring and ultrasonic oscillation. The ratio of graphene to sulfuric acid is 1:50 g/ml. Then nitric acid is added to the mixture, and the mixture is moved to an oil bath with 140 °C constant temperature, the volume ratio of sulfuric acid to nitric acid is 3:1. After 1 h magnetic stirring and condensation,

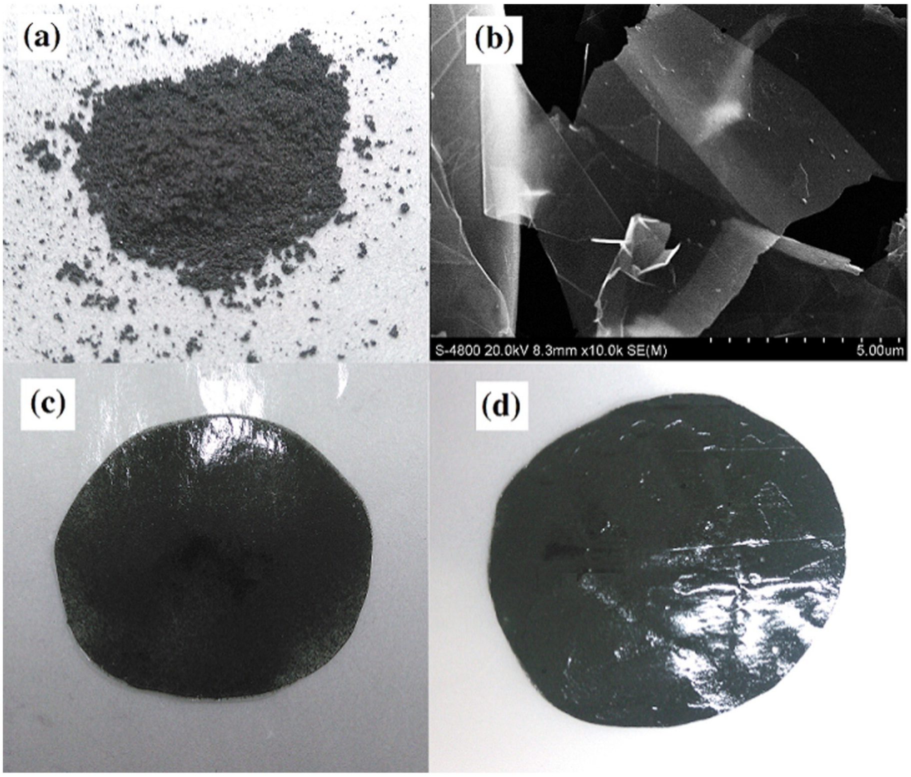

Fig. 1. The characterization of GHMPSA TIM. (a) Graphene source material; (b) SEM image of graphene from SCF Nanotech Ltd; (c) GHMPSA with 2 wt.% graphene; (d) GHMPSA with 5 wt.% graphene.

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