Journal of Nano- and Electronic Physics
Vol. **11** No 5, 05039(4pp) (2019)

Журнал нано- та електронної фізики
Том **11** № 5, 05039(4cc) (2019)

Effect of Graphene Nanoplatelet Concentration on the Thermal Conductivity of Silicone Thermal Grease

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(Received 03 May 2019; revised manuscript received 21 October 2019; published online 25 October 2019)

We herein report a facile route to improve the thermal conductivity of silicone thermal grease without deteriorating its conformability via exploitation of outstanding thermal conductivity and mechanical flexibility/ductility of graphene materials. The silicone thermal greases containing GNPs were prepared by using the high-energy ball milling process. The SEM images proved that GNPs were well dispersed in the base grease. The thermal conductivity of the thermal greases was investigated and presented. The obtained results demonstrated that GNPs are efficient for the thermal conductivity enhancement of the thermal grease. The highest thermal conductivity enhancement up to 59 % was obtained with the grease containing 0.75 vol. % GNPs. The enhancement could be attributed to high thermal conductivity of GNPs, the good compatibility and uniform dispersion of GNPs in the thermal grease. The thermal conductivity of the thermal grease with higher GNPs concentration of 1 vol. % was decreased due to the formation of GNPs clusters. By using Chu's model with the interfacial thermal resistance (R_k) fitting, we found that the thermal conductivity enhancement of the thermal grease concerns to the R_k between GNPs and the grease matrix. The best way to improve the thermal conductivity of the thermal grease is to reduce the R_k. The obtained results demonstrated the advantages of GNP in the thermal greases for the heat dissipation in high power electronic devices.

Keywords: Graphene, Silicone thermal grease, Thermal interface material, Thermal conductivity.

DOI: 10.21272/jnep.11(5).05039 PACS numbers: 65.60.+a, 65.80.+n

1. INTRODUCTION

Recently, the development of microelectronics and electronic nanotechnology, component density, power and speed of operation has increased rapidly. When the high power electronic components such as High Brightness LED (HB-LED) and Central Processing Unit (CPU) computer are generally being operated for a long time, energy will disappear and release amount of heat [1-3]. It is well-known that the reliability of high-power electronic devices is exponentially dependent on the operating temperatures, with which a small variation can result in two times reduction in the lifespan of a device [4, 5]. Therefore, the heat generated from high-power electronic devices should be dissipated as quickly and effectively as possible to maintain the operating temperatures of the devices at the desired level [6]. Accordingly, it is essential to develop well thermal management to extend the lifetime, enhance the efficiency, and ensure optimum performance and reliability of high power electronic components.

Traditionally, heat sinks have been used to dissipate heat released from electronic devices. However, the performance of a heat sink limited due to interfacial thermal resistance arising from the mismatch with non-surface flatness and surface roughness of both the devices and the heat sink [7, 8]. To increase the heat dissipation of high power equipment, thermal grease is considered as an ingenious solution. In general, thermal grease is classified as a thermal interface material (TIM) with good thermal conductivity, normally employed to fill the gaps of the mating surface more effectively [9-11]. Among various types, silicone thermal grease is considered as one of the most promising TIM, consisting of two main components, polymeric matrix and thermally conductive fillers [11, 12]. Many works have been done to enhance the thermal conductivity of silicone grease by adding the nanomaterials such as nanoparticles, nanotubes, nanosheets, etc. [13-16]. Recently, graphene is a two-dimensional nanocarbon material with the hexagonal packed structure compromised of sp2-hybridized carbon atoms, experimentally realized in 2004. Graphene has attracted intensive interest in many fields due to its exceptional physical and chemical properties, such as high electrical conductivity, superb thermal conductivity [17], and high mechanical strength. The superb thermal conductivity of graphene has opened a new window for application in the thermal grease for the heat dissipation of high-power electronic devices [18-22]. In this report, we focus on research of thermal grease containing GNPs by using silicone grease and high-energy ball mill method. The results showed an enhancement in thermal conductivity up to 59 % for grease containing 0.75 vol. % GNPs.

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2. MATERIALS AND METHODS

The graphene nanoplatelets (GNPs) with purity of 99.5 % purchased from ACS Material Company, USA were used as filler. Silicone thermal grease with the thermal conductivity of 2 W/m.K supplied by Hongda Chemical, China was used as matrix.

The fabrication process of silicone thermal grease containing GNPs is shown in Fig. 1. GNPs with different concentrations (0.25, 0.5, 0.75 and 1 vol.%) were milled with the silicone thermal grease by using high-energy ball mill process (8000D Mixer/Mill) at a speed of 8000 rpm for 3 hours to obtain the thermal grease containing GNPs.

Field-emission scanning electron microscope (FESEM) was used to examine the size, morphology, and distribution of GNPs in the thermal grease. Raman spectroscopy was used to analyze the structure of GNPs and thermal grease containing GNPs. Transient Hot Bridge THB-100 (Linseis, Germany) was used to measure the thermal conductivity of the grease in the range from 1 to 100 W/m.K at room temperature.

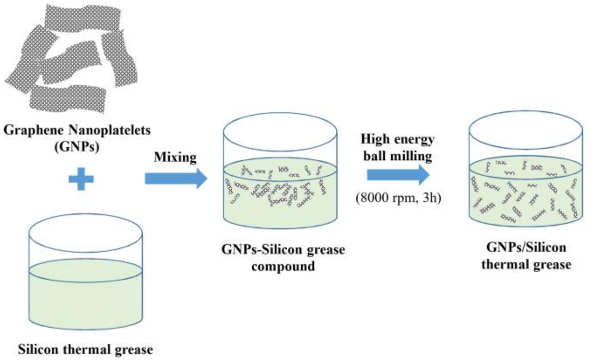

Fig. 1 – Schematic diagram of the fabrication process of silicone thermal grease containing GNPs

3. RESULTS AND DISCUSSION

Fig. 2 shows a typical FESEM image of the GNPs at high magnification. The thickness of nanosheets was in the range of 2-10 nm, the average diameter was about 5 μm with high cleanliness.

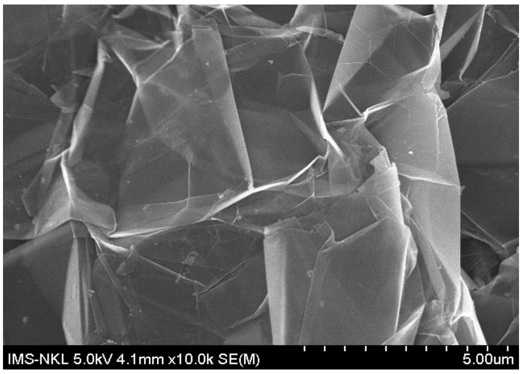

Fig. 2 – FESEM image of graphene nanoplatelets

Raman spectrum of the GNPs is shown in Fig. 3, revealing the most prominent features in the Raman spectra of graphene materials, including G (~ 1579 cm^{-1}) and 2D (~ 2687 cm^{-1}) bands. No D band (defective signature) is found in the spectrum, suggesting the high graphitic quality of the GNPs.

Fig. 4a shows the SEM images of thermal grease containing 0.75 vol. % GNPs as prepared. As can be seen, the silicone thermal grease used in this research contains some large and small filling particles distributed in the grease. In order to observe the distribution of GNPs and the compositions of grease, the sample was annealed at 300 °C for 3 h in vacuum to remove the organic binders. Fig. 4b shows the distribution of the metal oxide particles of the grease and GNPs inside thermal grease after annealing. This indicates that silicone grease clings to graphene. In other words, GNPs were good compatibility and well-dispersed in the silicone grease, thereby enhancing the thermal conductivity of grease.

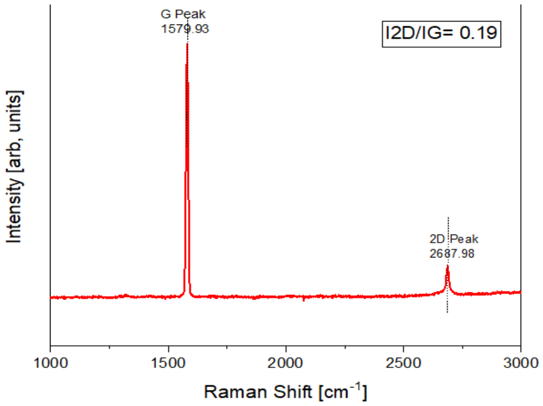

Fig. 3 – Raman spectra of GNPs

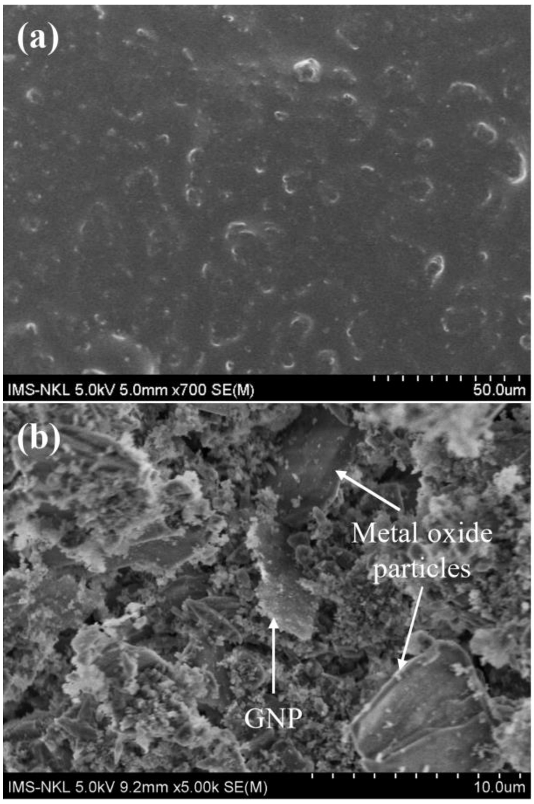

Fig. 4 – FESEM image of silicone thermal grease containing GNPs before (a) and after (b) annealing at 300 °C for 3 h in vacuum

Fig. 5 shows the thermal conductivity and the thermal conductivity enhancement of thermal grease with different GNP concentrations. In which, the thermal conductivity enhancement calculated using the equation is $(k - k_0)/k_0$, where k and k_0 are the thermal conductivity of the silicone thermal grease and the thermal grease containing GNPs, respectively. The thermal conductivity of silicone thermal grease containing GNPs was measured to be 2.18, 2.69, 3.14 and 2.53 W/m.K corresponding to the grease with 0.25, 0.5, 0.75 and 1 vol. % CNPs, those are much improved in comparison with pure silicon thermal grease (1.98 W/m.K). Similarly, the thermal conductivity enhancement was calculated to be 10 %, 36 %, 59 %, 28 % corresponding to the thermal grease containing 0.25, 0.5, 0.75 and 1.0 vol. %, respectively. It is interesting noted that the thermal conductivity enhancement is recorded with the GNP concentration up to 0.75 vol. % (59 %), then decreased as GNP concentration reached 1 vol. %. The enhancement could be attributed to the high thermal conductivity of GNPs. The decrease in the thermal conductivity of the grease with 1 vol. % GNPs could be due to the formation of GNPs clusters during the mixing process.

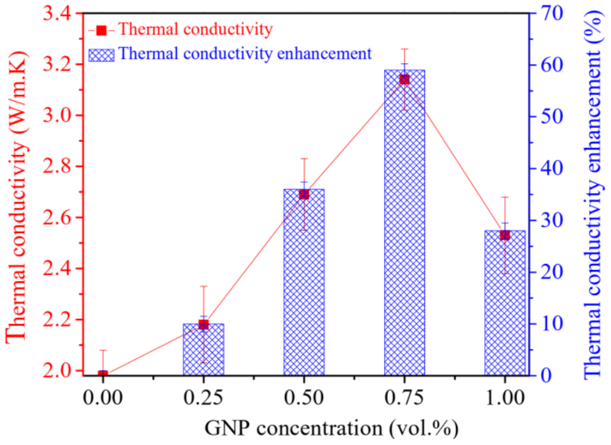

Fig. 5 – Thermal conductivity enhancement of silicone thermal grease containing GNPs with different concentrations

The thermal conductivity of the thermal grease not only depends on the thermal conductivity of filler, but also on the interfacial thermal resistance (R_k) between fillers and grease matrix. In this case, we have used Chu's model to estimate the R_k by fitting the experimental data and the calculated data. The model took into account the effects of the thickness, length, flatness of GNPs and R_k between GNPs and grease matrix. The model was expressed as the following equation (1):

$$\frac{k}{k_0}=\frac{3+2\eta^2\varphi/\left[k_0(2R_k/L+13.4\sqrt{t})\right]}{3-\eta\varphi}, \qquad (1)$$

where $\eta = 0.7$, $L = 2$ μm and $t = 5$ nm are the flatness ratio, the length, and thickness of GNP, respectively. $k_0 = 2$ W/m.K is the thermal conductivity of the silicone thermal grease. Fig. 6 shows the predictions of thermal conductivity enhancement as a function of GNP concentration compared with the experimental data using Chu's model with the variation of R_k. As can be seen, R_k decreased from $3.5 \cdot 10^{-9}$ mK²/W to $1.3 \cdot 10^{-9}$ mK²/W then to $1.1 \cdot 10^{-9}$ mK²/W corresponding to the grease containing GNP concentration of 0.25, 0.5 and 0.75 vol. %. The decrease of the R_k when increasing the GNP concentration in the thermal grease could be due to the improvement of the phonon interaction between GNPs. Besides, the good compatibility and uniform dispersion of GNPs in the thermal grease is also contributed to the decrease of the R_k. In contrary, R_k of the thermal grease containing 1 vol. % GNPs was calculated to be $4.9 \cdot 10^{-9}$ mK²/W. This value is much higher than those of the thermal grease containing lower GNP concentration. In this case, the increase of the R_k has mainly attributed to the formation of the GNPs clusters as resulted from the π-π stacking during the mixing process. As obtained results, we can conclude that the decrease of the R_k between GNPs and matrix is the best way to improve the thermal conductivity of the thermal grease. This can be done by improving the bonding between GNPs and matrix via functional groups and also prevent the formation of GNPs clusters.

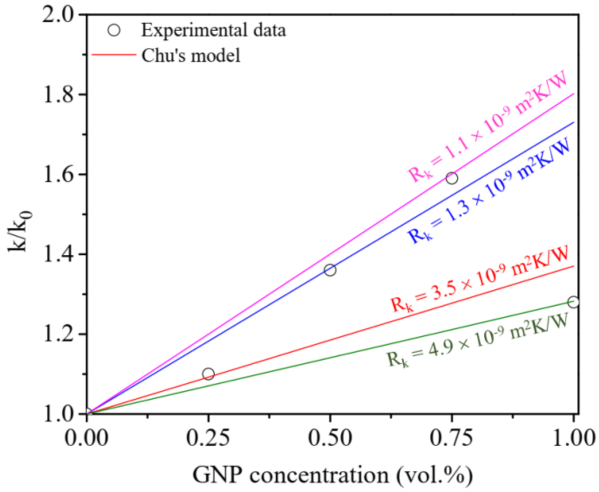

Fig. 6 – Chu's model predictions of thermal conductivity enhancement as a function of GNP concentration compared with the experimental data

4. CONCLUSIONS

We have successfully fabricated the silicone thermal greases containing GNPs. The SEM images proved that GNPs are dispersed in the based grease by high energy ball mill method. The thermal conductivity of the thermal greases was investigated. The measured results showed that GNPs are efficient for the thermal conductivity enhancement of the thermal grease. The highest thermal conductivity enhancement up to 59 % was obtained with the grease containing 0.75 vol. % GNPs. The obtained results confirmed the advantages of GNPs in use as filler in the thermal grease for the heat dissipation of high power electronic devices.

ACKNOWLEDGEMENTS

The research was financially supported by the Fostering Innovation through Research, Science and Technology (FIRST) under grant No. 16/FIRST/1a/IMS.

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Вплив концентрації графенових нанопластинок на теплопровідність силіконової термопасти

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Ми повідомляємо про ефективний шлях до підвищення теплопровідності силіконової термопасти без погіршення її сумісності за рахунок використання високої теплопровідності та механічної гнучкості/пластичності графенових матеріалів. Силіконові термопасти, що містять графенові нанопластинки (ГНП), готувалися із застосуванням високоенергетичного помелу в кульовому млині. Зображення СЕМ показали, що ГНП були добре дисперговані у базовій термопасті. Досліджена теплопровідність термопасти. Отримані результати показали, що ГНП ефективні для підвищення теплопровідності термопаст. Найвище підвищення теплопровідності до 59 % було отримано для термопасти, що містить 0,75 об. % ГНП. Таке підвищення можна віднести до високої теплопровідності ГНП, хорошої сумісності та рівномірного диспергування ГНП у термопасті. Теплопровідність термопасти з більш високою концентрацією ГНП 1 об. % зменшувалася за рахунок утворення кластерів ГНП. Використовуючи модель Чу з підбором міжфазної термостійкості (R_k), ми виявили, що підвищення теплопровідності термопасти стосується термостійкості R_k між ГНП та матрицею термопасти. Найкращий спосіб поліпшити теплопровідність термопасти – це зменшити R_k. Отримані результати продемонстрували переваги ГНП в термопастах для розсіювання тепла в електронних пристроях високої потужності.

Ключові слова: Графен, Силіконова термопаста, Тепловий матеріал інтерфейсу, Теплопровідність.