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Enhancement of commercially-available thermal grease by multiwalled carbon nanotubes for electronic device applications

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ABSTRACT

Thermal grease is generally used as a thermal interface material for improved conduction between a heat source and heat sink. Here, we report the enhancement of thermal conductivity of commercially available off-the-shelf thermal grease (thermal compound LS6006) used in cooling of electronic devices, by the addition of multiwalled carbon nanotubes (MWCNTs). The thermal conductivity of the MWCNT mats and MWCNT modified thermal grease was measured relative to the thermal conductivity of the grease, which was taken as the benchmark. The thermal conductivity improves and the optimum thermal management is observed for aligned MWCNT arrays glued through the thermal grease.

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Introduction

The work on thermal interface materials is essential as poor thermal conduction between heat source and a heat sink would make the use of expensive and large heat sinks inefficient [**1, 2**]. Thermal interface materials are commonly used as an intermediate material in the thermal management of many electronic devices. Used as an intermediate between the heat source and heat sink, it improves the thermal conductivity, thereby improving the heat dissipation. Generally, these materials are thermo-viscous in nature, which helps them spread out evenly as the temperature increases, and cover pores and unevenness. Efficient thermal management of electronic devices is important for better performance and longevity of the devices [**3**].There is a continuous need for developing cooling methods and materials that can dissipate heat in a more efficient manner. Carbon nanotubes (CNTs) should be ideal for high-performance thermal management as the thermal conductivity is superior to other materials [**4-6**] and has been exploited mainly in improving the thermal management of high power electronics [**7**]. It has been shown that single walled CNTs (SWCNTs) can be mixed with an epoxy to improve the thermal management [**6**] or can be used directly [**7**].

In a process to augment the thermal properties of thermal grease, thermal conductivity of SWCNT modified grease has been investigated at low temperature [**7**]. In this work, we have replicated the setup of a computer processor and investigated the relative enhancement of the off-the-shelf thermal grease (thermal compound LS6006) by adding multiwalled CNTs (MWCNTs) to it, and investigated the thermal transport properties above room temperature. The advantage of using a paste rather than direct growth of MWCNTs is the ease in application and use of the paste. The thermal grease was modified by adding 1%, 2% and 4% of MWCNTs and evenly mixing it till a uniform color change was noted from gray to black. A mat of aligned MWCNTs and MWCNT grown on copper were also tried as interface materials.

Experimental

To investigate the enhancement in the thermal conductivity, we tried to replicate the setup of a computer processor for the experiment. The experimental setup used is shown in **Fig. 1 (a).** The setup consisted of a heat source, a hot plate (in place of the transistors that produce heat in processors), an integrated heat spreader (IHS), generally used on processors. A copper foil was placed on top of the IHS acted as the temperature measurement point. The thermal grease/MWCNT mats were sandwiched between the IHS and the copper foil. A K-type thermocouple was used to measure the temperature, which was connected to a Keithley 2182A nano-voltmeter. The temperature readings were noted every 30 seconds. The readings were recorded starting at room temperature, to a peak temperature. The hot plate was turned off when the temperature reached 100

^{0}C. After that, the temperature continued to rise till it reached a peak. To keep the calculation uniform, the heating temperatures were considered from 5 minutes after the start of the experiment, as there was a slight variation in the room temperature. In **Fig. 1(b)**, R_g indicates the thermal resistance at the interface between IHS/thermal grease and thermal grease/copper foil.

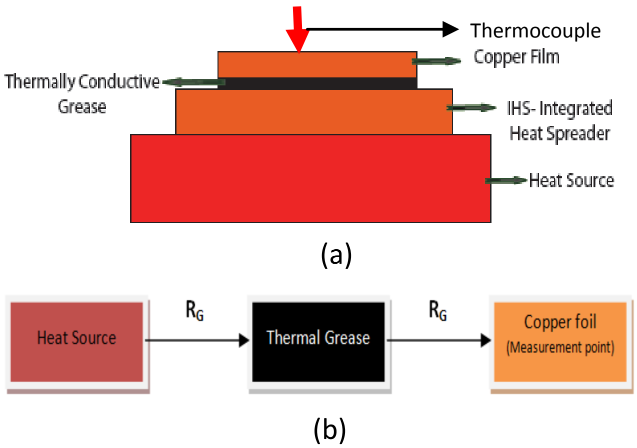

Fig. 1. (a) Replica of the experimental setup and (b) Resistance network.

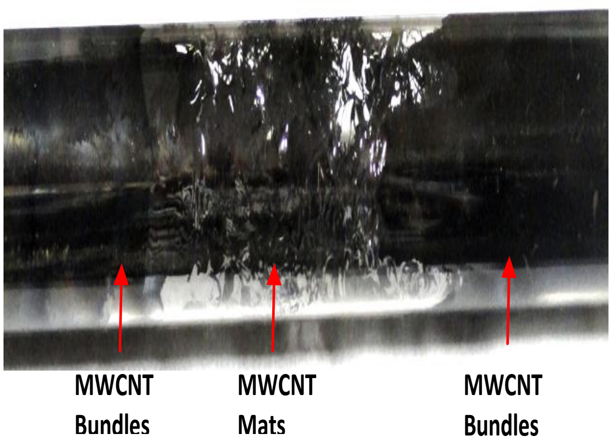

Fig. 2. Quartz tube with MWCNT bundles and mats.

The synthesis of MWCNTs is by one-step pyrolysis [**9**]. In brief, the method used to grow MWCNT is a one-step method in which ferrocene and benzene are taken in a quartz tube closed at one end and a bladder fixed at the other end and is heated to a temperature of 950 ^{0}C for 4 h after which, MWCNTs are obtained in the form of mats and bundles [**9**]. **Fig. 2** shows the quartz tube with the growth of the MWCNT deposited on the walls of the quartz tube. The MWCNT were also grown directly on copper foil. A clean copper foil was placed the in tube, which led the MWCNT to be deposited on the foil.

Both bundles of MWCNT as well as mats were obtained depending on the position of the quartz tube in the furnace[9]. Both bundles and mats produced using this method were used in the experiment. The bundles were disperssed in the grease, while the mat was used as such. **Fig. 3(a-d)** show the SEM images of 1%, 2%, 4% MWCNTs added to the grease respectively and MWCNT aligned arrays. The MWCNT bundles can be observed throughout the matrix.

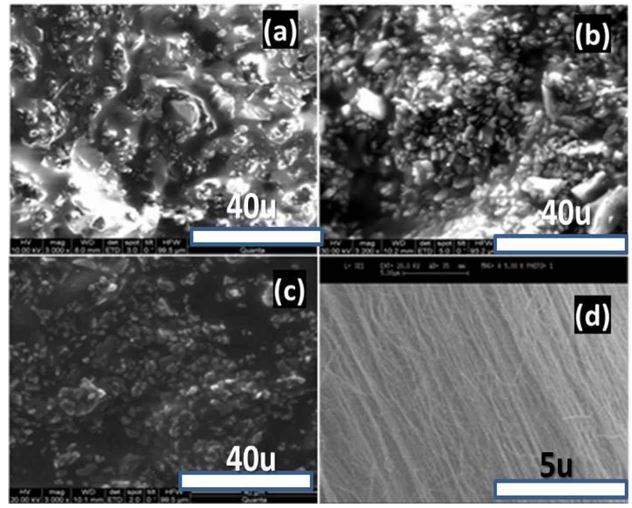

Fig. 3. SEM images of grease with (a) 1%, (b) 2%, (c) 4% and (d) aligned MWCNT bundle.

Results and discussion

Fig. 4 shows the variation of the temperature during heating. The thermal grease has been used as the benchmark, and the change in performance of all the other materials are compared to it. This entire setup and procedure was kept consistent for the entire experiment. So, as the resistance of this grease reduces due to the addition of MWCNT, the amount of heat flowing from the source to the sink should increase. This is reflected in the results shown in **Fig. 4** and **Table 1**. Also indicated in **Fig. 4** is a line at 100 ^{0}C which indicates where the hotplate was turned off in each experiment.

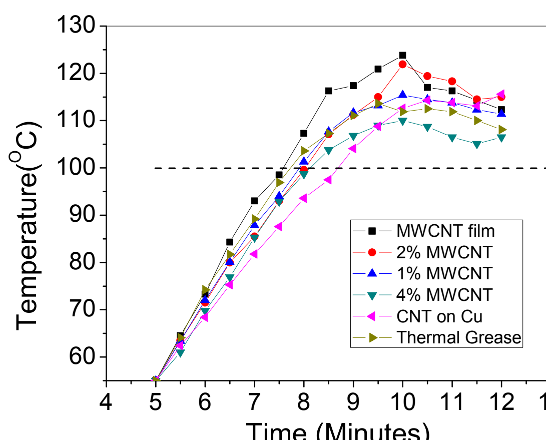

Fig. 4. Variation of temperature during heating.

The rate of dissipation was calculated using the relation-

$$X_{heating}=(T_{peak}-T_{5min})/(t_{peak}-5) \qquad (1)$$

where, T represents the temperature and t is the time. Table I compares the rate of dissipation for grease, (grease + MWCNT) mixture and MWCNT mat. As can be seen from the plot, MWCNT mat had the highest rate of dissipation, and the MWCNT grown on copper had the slowest rate. This indicates that the MWCNT mat showed the best performance and the MWCNTs grown directly on the copper foil had the least performance. As it can be seen from **Fig. 4** & **Table 1**, the best result is obtained for the MWCNT mat, which is considerably higher than the next best result for thermal grease with 2% MWCNTs.

Table 1. Relative thermal conductivities (K_H) and rate of heat dissipation of different materials.

Material	Relative thermal conductivity (K_H)	Rate of heat loss	Start temp T_0	Peak temp T_1	Peak -start temp (T_1-T_0)
Grease	1	9.55 °C /min	63.7 °C (t=5)	125.8 °C (t= 11.5 m)	62.1°C (6.5 min)
MWCNT Mat	1.44	13.7 °C /min	70.7 °C (t=5)	139.5 °C (t= 10)	68.8 °C (5 min)
1% MWCNT	1.26	12.1°C /min	62.2 C (t=5m)	122.7 °C (t=10 m)	60.5 °C (5 min)
2% MWCNT	1.40	13.3 °C /min	55 °C (t=5)	121.9 °C (t=10 m)	66 .9 °C (5 min)
4% MWCNT	1.13	10.8 °C /min	67 °C (t=5m)	121 °C (t=10 m)	54 °C (5 min)
MWCNT on Copper	0.90	8.6 °C /min	55 °C (t=5m)	115.6°C (t=12 m)	60.6 °C (12min)

The relative thermal conductivity were evaluated using the relation-

$$K_1(a/l)\Delta T_1 = K_H(a/l)\,\Delta T_2 \qquad (2)$$

where K_1 is the conductivity of the grease, which was taken as benchmark, K_H is the thermal conductivity of the modified paste, a is the area and the l is the distance between IHS and the upper copper foil. Utmost care has been taken to keep both a and l the same so that the term (a/l) is cancelled out in all cases. Taking K_1=1, we calculated K_H in terms of K_1. **Table 1** compares the relative thermal conductivity of the different materials compared to

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From **Table 1,** it can be observed that the MWCNT mat reaches its peak temperature of 139.5 °C (68.8 °C in 5 minutes), compared to the grease which reaches its peak temperature of 128.5 °C (62.1°C in 6.5 minutes). It can also be observed from **Table 1** that the rate of heat gain increased when the concentration of the MWCNT was increased from 1% (60.5 °C gain in 5 minutes) to 2% (66.9 °C gain in 5 minutes). But when the quantity of MWCNT was increased to 4%, the conductivity began to drop (54°C gain in 5 minutes). A plausible explanation is the non-alignment of MWCNTs in the grease as it is mixed by hand until a uniform color changed was noticed. As the amount of MWCNTs added was increased, the random scattering of the MWCNTs in the grease increased, causing scattered flow of heat through the grease matrix, and as a consequence decreased the thermal conductivity. It can also be observed that, although the rate of heat flow reduced when the amount of MWCNT was increased from 2% to 4%, the performance of 4% MWCNT+grease was still better than the plain grease (100%Grease+0%MWCNT). The improvement of thermal transport properties is believed to be due to the MWCNT dispersed in the thermal grease. Similar peak temperatures and the time taken to reach them are indicated in the last column of **Table 1**.

As indicated in **Fig. 1(b)**, the thermal resistance affects the heat dissipation, which was reduced by the addition of the MWCNT. From **Fig. 1(b)**, it can be understood that as the resistance R_G reduces, the rate of heat dissipation increases. The last column in **Table 1** indicates (Peak-Start) temperature (T_1-T_0). This column indicates both temperature gain (the difference in the peak and start temperatures) and the time taken to achieve the peak temperature. Initially, comparing the unmodified grease (0%MWCNT+100% grease) with the MWCNT mat (100% cnt + 0% grease) it can be observed that the grease took 6.5 minutes to reach a peak temperature of 128.5 °C (a gain of 62.1 °C in 6.5 minutes) and the MWCNT took 5 minutes to reach a peak temperature of 139.5 °C (a gain of 68.8 °C in 5 minutes). This indicates that the resistance R_G between the heat source and the measurement point reduced, leading to the faster heat gain. This is because the grease has a lower thermal conductivity compared to the MWCNT mat. Similarly, from the 1% and 2% MWCNT readings, it can observe that, the 1% MWCNT took 5 minutes to reach a peak temperature of 122.7 °C (a gain of 60.5 °C in 5 minutes) and the 2% MWCNT took 5 minutes to reach a peak temperature of 121.9 °C (a gain of 66.9 °C in 5 minutes). This again indicates that the resistance R_G between the heat source and the measurement point reduced more in the case of 2% MWCNT, hence causing the faster raise in temperature. The results in **Table 1** are indicative of the fact that as there is a reduction in thermal resistance R_G, the amount of heat flowing from the source to the point of measurement (thermal conductivity) increases.

The first row of **Table 1** indicates the heat loss rate, start temperature, peak temperature, and the (peak-start) temperature of the thermal grease. This reading was taken as the benchmark and all other thermal conductivities were calculated relative to the grease (thermal conductivity taken as 1). **Table I1** also indicates relative thermal conductivity of each material. In the case of the MWCNT mat the result was $K_H = 1.44\ K_1$ which indicates that the 44% more power is dissipated through MWCNT mats as compared to 11% power dissipation through MWCNT fin structures [**8**]. It may be noted the fin structures were soldered on the chips. To get better adhesion, the thermal grease was used on both the sides of MWCNT mats and the MWCNT on copper in our investigation. This was done to ensure optimal contact between the IHS and the mat, so that the contact resistance between them would be low.

Considering the relative thermal conductivity, if we take a closer look at **Table 1**, the MWCNT mat showed the best results, reaching the highest peak temperature fastest, with $K_H = 1.44K_1$, meaning, the MWCNT mat was 1.44 times better than the thermal grease during heating (K_H). This is very much comparable to the results obtained for carbon fiber loading in the epoxy [**5**]. Looking at the other results, the 1%, 2% and 4% MWCNT+grease samples, all of these showed considerable improvement in the heating cycle compared to the thermal paste ($K_H > 1.26K_1$, $1.40K_1$, $1.13K_1$ respectively). This was expected considering the fact that MWCNT mats have much higher thermal conductivity. **Table 1** indicates that the relative thermal conductivity of MWCNT was the highest among all the materials used.

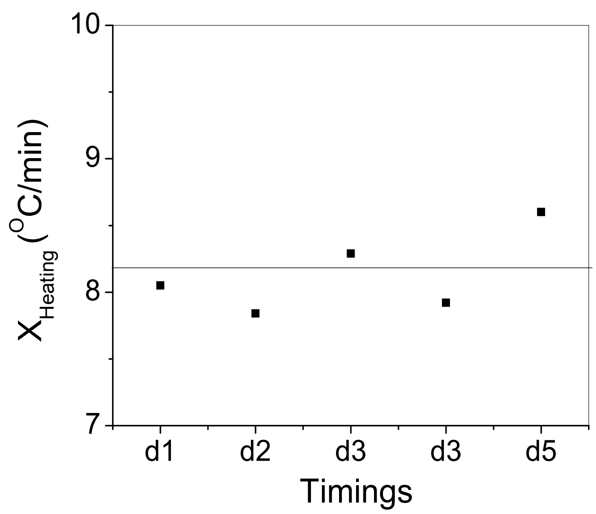

Fig. 5. Fatigue test for rate of heat dissipation

Another observation that was made was, as the amount of MWCNTs was increased from 1% to 2% the efficiency of the paste went up from $K_H = 1.26K_1$ to $K_H = 1.40K_1$. But when this amount was increased to 4%, the efficiency fell to K_H=1.13 from K_H= 1.40. This indicated that for this experiment 2% MWCNTs was close to the ideal amount to add to the grease to get the best performance (this was the best thermal conductivity for grease + MWCNTs).

The last material to consider is the MWCNTs grown on a copper foil. As it can be seen from the table and the plot, it had the lowest performance. One of the plausible explanations for this could be the formation of an oxide layer between the MWCNTs and the copper foil. The formation of copper oxide takes place at a lower temperature compared to the temperature needed for the growth of MWCNTs [**9,10].** Therefore, the growth of the MWCNTs would have taken place on copper oxide, leading to lower performance.

In order to check the stability of the greases, several readings were taken for each material at different times of the day, and with few days interval to check for the consistency of the material over continuous use, as well as to check if storing it over a period of time would cause any degradation or hardening of the grease matrix causing a change in the thermal conductivity of the prepared MWCNT mixed grease. The data obtained showed consistency, an average of 0.5 degrees of difference in the rate of heating was observed indicated in **Fig. 5** (day 1 = d1 day 2 = d2, day 3 = d3 and so on).

Another interesting observation was made. When th hotplate operating temperature was raised above 220 ^{0}C and allowed to cool, the grease seemed to became thicker, while the MWCNT mats remained unaltered and intact. These were just observations and no actual measurements were made for the change in viscosity (although, the change was visually apparent).

Conclusion

In summary, we have modified the commercial thermal grease LS-6006 by the addition of MWCNT that showed improvement in thermal conductivity of the grease. However, the amount of MWCNTs cannot be increased as a drop in the thermal conductivity was noticed for 4% of MWCNTs. The best performance was obtained by a mat of MWCNTs compared to the thermal grease or modified thermal grease. Better results can be obtained if the alignment of the MWCNTs can be controlled during the modification of the grease. There is scope for achieving better thermal conductivity by modifying the setup and controlling all the variables involved.

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Reference

1. Y. Xu, C. K Leong and D. D. L Chung, J. Elelc. Mat. 36, 1181 (2007).
2. Sashi K C, B Harris, J. W. Hiestand, Proc. ASME Intl. Mech. Engg. Cong. Expo. 38827 (2010).
3. M. Stan, K. Skadron, M. Barcella, W. Huang, K. Sankaranarayanan and S. Velusamy, Microelectronics J. 34, 1153 (2003).
4. A. Shakouri, Proc. IEEE, 94, 1613 (2006)
5. H.-Y. Chiu, V.V. Deshpande, H.W. Ch. Postma, C. N. Lau, C. Miko, L. Forro and M. Bockrath, Phys. Rev. Lett. 95, 226101 (2005).
6. P. Kim, L. Shi, A. Majumdar and P. L. McEuen, Phys. Rev. Lett. 87, 215502 (2001).
7. M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun and A. T. Johnson and J. E. Fischer, Appl. Phys. Lett. 80, 2767 (2002).
8. K. Kordás, G. Tóth, P. Moilanen, M. Kumpumäki, J. Vähäkangas, A. Uusimäki, R. Vajtai and P. M. Ajayan, Appl. Phys. Lett. 90, 123105 (2007).
9. P. Mahanandia and K.K. Nanda, Nanotechnology 19, 155602 (2008).
10. S. C. Vanithakumari, S. L. Shinde and K. K. Nanda, Mat. Sci. Eng. B 176, 669 (2011).