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ARTICLE

AlN/Ga-based Liquid Metal/PDMS Ternary Thermal Grease for Heat Dissipation in Electronic Devices

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Abstract: A new composite thermal interface material (TIM) was synthesized by combining AlN with liquid metal (LM, $Ga_{68.5}In_{21.5}Sn_{10}$) and polydimethylsiloxane (PDMS), one of the most commonly used silicone oils, to enhance the interfacial heat transfer. The microstructure and chemical composition of the material were analyzed using scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS) to investigate its principle of heat dissipation. The thermal conductivity (κ) of the AlN liquid metal thermal grease (ALTG) was found to be 5.014 W/m·K, higher than that of a liquid metal/PDMS composite (LMTG) and higher than that of one of the best existing thermal grease products (X23-7762) by approximately 5% and 20%, respectively. Meanwhile, the thermal contact resistance (R) was reduced by 20% and 50%, respectively, and the viscosity remained in an appropriate range, reducing the risks of overflow during usage. An actual test on a CPU showed that ALTG could significantly reduce the operating temperature. The thermal mechanism of ALTG was studied, and a synergistic effect was suggested for the heat transfer process. The results prove the ideal heat dissipation properties of TIMs and their wide application prospects in industry.

Key words: Ga-based liquid metal; AlN; thermal grease; heat transfer enhancement

With the rapid reduction in the size of electronic devices and systems, heat dissipation has already emerged as a critical problem that impedes the performance and reliability of these devices[1,2]. Due to the limitations of the manufacturing process, even a very smooth surface-to-surface contact between a CPU and a heat sink will inevitably have certain gaps, and the presence of these voids will severely affect heat dissipation. Traditional underfills and TIMs are mainly composed of polymers and inorganic fillers (e.g., metal particles, BN, AlN, nanoclays, carbon nanotubes), which fill in these gaps to ensure good contact, increase the contact area, and ultimately improve the heat transfer efficiency. Polymer material is used as the matrix, and the κ value is improved by adding thermally conductive particles. However, these traditional TIMs are still generally poor in κ and cannot meet the needs of high-performance electronic components[3].

In the filler material sector, graphene has been widely used because of its ultra-high thermal conductivity[4,5]. However, its high price and complicated preparation process impede its use as a good TIM filler. Because of its excellent thermal conductivity (380 W/m·K), good insulation properties and low price, AlN also has good application prospects as a thermal filler for use in composite thermal materials[6]. At the same time, in view of the shortage of the above TIMs, increasing attention has been paid to liquid metals as TIMs because of their flexibility, relatively high thermal conductivity, and low resistance[7]. Martin et al. showed that the resistance of an LM-based TIM could be reduced to a minimum of 2 mm^2·K/W. In addition, the stress caused by different thermal expansion coefficients between the silicon chip and the heat sink can be effectively mitigated[8]. Webb demonstrated that the thermal resistance of an In-Bi-Sn alloy TIM was 5.8 mm^2·K/W at a contact pressure of 138 kPa[9,10]. However, two unfavorable factors when a liquid metal is used as a TIM remain to be resolved: oxidation during usage, which will lead to a decline in performance, and the strong fluidity of liquid metal, which poses a risk of leakage.

To address the above problems, in this study, we attempted

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to synthesize a novel TIM through simple methods. We added liquid metal and AlN into PDMS. The results showed that the new material can achieve a great improvement in thermal conductivity compared with one of the best commercially available thermal grease products, X23-7762. Finally, experiments demonstrated it to be an ideal heat dissipation material for a high-performance CPU; it lowered the temperature by 4 °C more than a commercial thermal silicone pad. Since all of the raw materials we used are non-toxic and simple to produce, this new TIM is a promising heat dissipation material for use in future devices.

1 Experiment

1.1 Preparation of samples

The starting materials are as follows.

PDMS: polydimethylsiloxane Sylgard 184, viscosity 500 mPa·s (Dow Corning Corporation, USA); AlN powder (AR>99%): particle size 3 μm (Desunmet Ceramic Material Co. Ltd, Tieling, China); Ga, In, and Sn powders (Hebei Promotec Metal Master Technology Ltd., Chengde, China); industrial-grade multi-layer graphene: thickness 5 nm (Suzhou Hengguo Graphene Technology Co., Ltd, Suzhou, China).

Liquid metal was prepared from Ga (68.5 wt%), In (21.5 wt%), and Sn (10 wt%) [11]. The gallium was placed in a flask immersed in a water bath at 50 °C. Then, indium and tin were added into the gallium-loaded flask. Under a protective argon atmosphere, this mixture was stirred with rods until the indium and tin had fully compatibilized with the liquid and was mixed well for 10 min. This procedure yielded the Ga-based alloy known as Galinstan, which has a low melting point of approximately 12 °C.

Galinstan was added to a beaker containing PDMS at a Galinstan:PDMS mass ratio of 5:1 until all liquid metal was encapsulated in the polymer, and the mixture was then stirred for 20 min to ensure sufficient mixing[12,13]. Thus, the first TIM, referred to as liquid metal thermal grease (LMTG), was prepared. In a similar way, a mixture with an LM:PDMS:AlN mass ratio of approximately 25:4:1 was prepared to obtain the second TIM, referred to as AlN liquid metal thermal grease (ALTG). For comparison, a graphene liquid metal thermal grease (GLTG) with the same mass ratio was prepared. The procedure is shown in Fig.1.

1.2 Characterization

Inspection of the samples: The interfaces of the samples and the chemical composition were evaluated via SEM using a Japan Electronics JSM-6360 scanning electron microscope (30 kV, magnification: 7~1 000 000) and an energy dispersive spectrometer (EDS: Al, 20 kV) [14].

Thermal properties (κ and R) and viscosity: The DZDR-S (Nanjing Grand Electro Mechanical Co., Ltd., Nanjing, China) is a thermal conductivity tester based on the modified transient plane source (TPS) technique with a range of 0.005~300 W/(m·K). The equipment was placed in a constant-temperature and humidity test room at 25 °C. Before each measurement, the heat conducting samples were placed in beakers for 1 h in the test room to reach equilibrium. During measurement, a planar spiral probe of a suitable size was inserted into each paste sample. This probe is both a heat source and a sensor (accuracy: 0.01 °C), which can detect the change in the voltage on the probe based on the Wheatstone bridge principle, and the data thus collected are sent to the host computer software to obtain the thermal conductivity (κ). In practice, the equipment provides a minimum probe diameter of 7.5 mm; as long as the size of the heat conducting material is greater than this diameter, good contact can be ensured. Since the dissipation effect of a TIM is affected by both κ and other factors, κ alone is not sufficient to fully describe the performance of such a material[15]. The T3Ster thermal transient tester (Mentor Graphics, UK), with a similar working principle and environment to those of the DZDR-S, was used to measure the thermal contact resistance (R) of our samples by analyzing the transient temperature response curve. To ensure the reliability of the thermal parameters, we tested every sample several times to reduce the influence of experimental error. The final statistics for each sample were calculated as the average of four values without obvious deviations.

For a TIM product, a suitable viscosity is required[16]. An excessively low viscosity makes a TIM unstable and increases

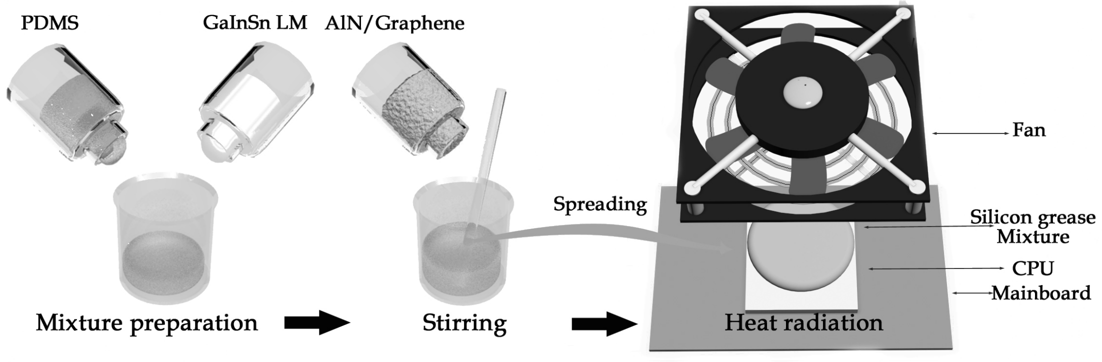

Fig.1 Synthesis of the TIM samples

the risk of leakage and overflow; an excessively high viscosity leads to adverse effects on the usage and manufacture. The NDJ Rotational Viscometer (Balance Instrument Technical Co., Ltd., Shanghai) was used to measure the viscosity.

Actual test on a CPU: The four TIMs described above were each applied to a CPU of X1 Carbon. Then, the program Prime95 was run on the computer as a stress tester, causing the CPU (Intel I55337U) to constantly operate at 100% capacity[17]. The CPU produced a large amount of heat, enabling a comparison of the heat dissipation properties of the 4 TIMs. Computer test software (AIDA64) was run for 30 min at the ambient temperature of 25 °C to generate the temperature vs. time curve. Moreover, the temperature distribution on the keyboard panel surface was obtained using a FLUKE infrared thermal imager.

2 Results and Discussion

2.1 Microscopic characterization of materials

SEM images and EDS spectra of the four samples are shown in Fig.2 and Fig.3, respectively. As shown in Fig.2a, the appropriate use of filler with different particle sizes can enable filling to the greatest possible extent. Fig.2b shows a microscopic image of the liquid metal/PDMS composite (LMTG). The surface of a pure liquid metal should be clean and smooth. After inevitable oxidization during the stirring process, folds appeared on the surfaces of some metal droplets, and a large number of solid particles formed during agitation[18]. The maximum diameter of the dispersed droplets is approximately 50 μm, but most of them are less than 20 μm at maximum filling. Obviously, the shape of the metal droplets is irregular and non-spherical, and the droplet formation results in a large number of voids filled with low-κ PDMS, interfering with the ability to form thermal paths through metal-to-metal contacts. Fig.2c shows the superiority of ALTG. The thermally conductive fillers are widely and evenly dispersed in the matrix material, forming thermal conduction paths via overlapping metal droplets, thereby making up for any defects in filling quantity to obtain higher thermal conductivity. Meanwhile, the addition of fillers reduces the flow of LMTG, causing the ALTG to act as a paste and thus resolving the problem of overflow. Fig.2d shows an image of GLTG. Since the color of the graphene is similar to that of the background, the structure is less visible, but it is clear that a similar synergistic effect occurred between the fillers.

Fig. 3 shows the elemental composition and contents of the 4 TIMs. Fig. 3a indicates that the traditional X23-7762 thermal grease is probably manufactured by adding high-κ particles such as Al_2O_3, ZnO and the like to PDMS. Fig.3c reflects the preparation of ALTG as a ternary TIM by adding AlN powder to LM/PDMS (Fig. 3b). After the similar addition of graphene to LM/PDMS to form GLTG, the number of observed element peaks does not change, as seen in Fig. 3d, but the C peak value is stronger in Fig. 3d than in Fig. 3b.

2.2 Thermal properties and viscosities

Table 1 lists the thermal properties and viscosities of the TIM samples as determined through testing. Sample 1, X23-7762, shows κ and R values of 4.206 W/m·K and 27 mm^2·K/W, respectively, consistent with the product specifications (4~4.5), demonstrating that the DZDR-S could accurately measure the thermal parameters. The contact thermal resistance of a TIM is mainly caused by the air gap between the heat transfer medium and the heat source (all R values listed above were statistically tested under 150 kPa). Sample 2, LMTG, yields κ and R values of 4.789 W/m·K and 18 mm^2·K/W.

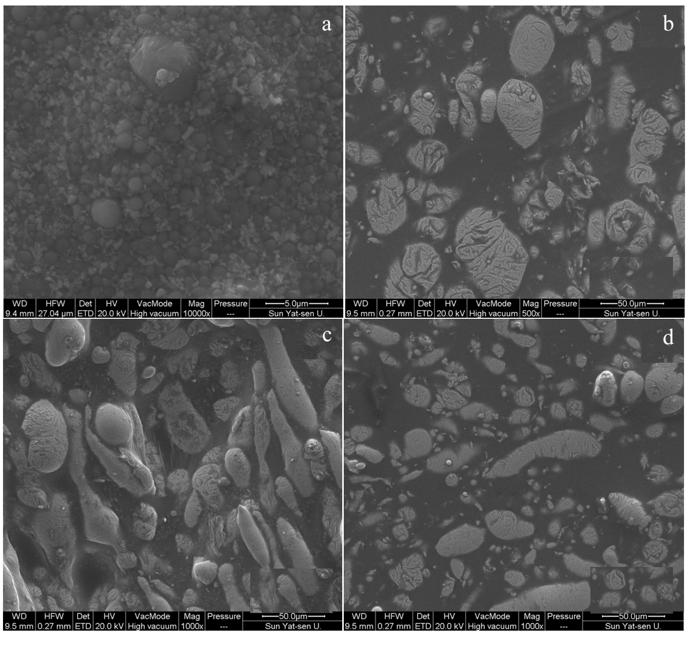

Fig.2 SEM images of X23-7762 (a), LMTG (b), ALTG (c), and GLTG (d)

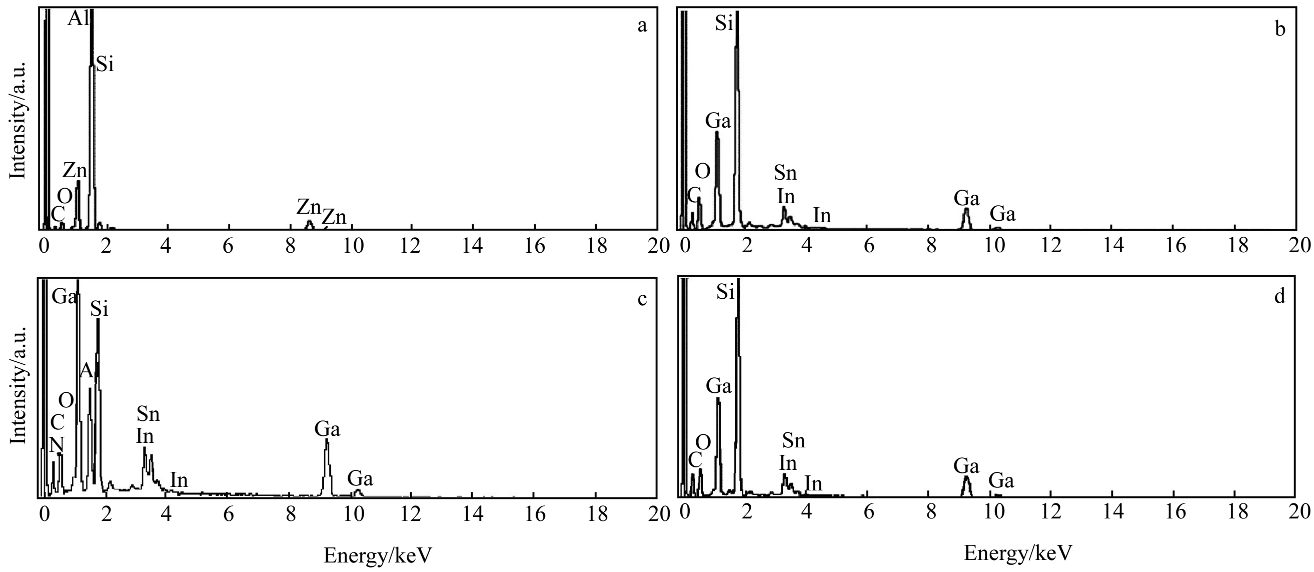

Fig.3 EDS spectra of X23-7762 (a), LMTG (b), ALTG (c), and GLTG (d)

Table 1 Results of thermal properties and viscosities of samples

No.	TIM	Thermal conductivity, κ/W·(m·K)$^{-1}$	Thermal resistance, R/mm^2·K·W^{-1}	Viscosity/Pa·s
1	7762	4.206	27	180
2	LMTG	4.789	18	35
3	ALTG	5.014	15	197
4	GLTG	4.961	16	217

The thermal conductivity of LMTG is significantly greater than that of the conventional grease, by 14%, and the contact thermal resistance is also reduced by approximately 34%. The findings show that using liquid metal as an additive to PDMS can effectively improve the thermal conductivity of the TIM and facilitate heat dissipation. Sample 3, ALTG, shows κ and R values of 5.014 W/m·K and 15 mm^2·K/W, respectively. Sample 4, GLTG, serves as a reference and shows κ and R values of 4.961 W/m·K and 16 mm^2·K/W, respectively. The thermal conductivities of the ternary thermal grease mixtures are approximately 20% higher than that of the best traditional grease, X23-7762, and nearly 5% higher than that of the liquid metal/PDMS composite. Its κ value above 5 W/m·K is sufficient to make ALTG one of the most excellent grease products developed to date. The contact thermal resistance also shows a significant decrease. According to the test results, the κ values of ALTG and GLTG are obviously higher than those of the other two samples, indicating greatly improved heat transfer performance at a solid-solid interface.

Regarding viscosity, the results show that the viscosity of LMTG is far lower than those of other materials. Compared with a traditional silicone grease with insulating fillers, this low viscosity causes LMTG to be more prone to leakage during use, resulting in possible loss of contact and adversely affecting the thermal environment. With the addition of high-κ fillers such as AlN particles, however, these particles become dispersed in the gaps between the components of the binary mixture and form more compact thermal conduction paths, thereby simultaneously improving the thermal conductivity and reducing the flowability of the grease. As shown in Fig. 2, the ternary mixtures ALTG and GLTG both became pastes, thereby effectively solving the problem of leakage. Since graphene fillers are more likely to achieve a high level of filling, excess sheets will tend to come free of the mixture. Although κ is improved, a significant increase in viscosity will also occur, resulting in practical difficulties. Thus, only ALTG successfully exhibited both a suitable viscosity and higher thermal properties.

Here, a successful previous study should be also mentioned. A binary thermal grease with a high thermal conductivity and viscosity was made by mixing oxidized liquid metal and PDMS[11]. The highest liquid metal volume fraction reached 81.8%, with a thermal conductivity of 5.27 W/(m·K); however, liquid metal droplets were found to leak out when the thickness of the coating was very thin during our tests. In ALTG, this phenomenon is effectively reduced, but it will be necessary to achieve further improvements in thermal conductivity to match this previous thermal conductivity performance.

2.3 Actual test on a CPU

The reference TIM X23-7762, developed by Shin-Etsu

Corporation, is one of the most widely used high-end thermal greases for all kinds of high-end notebook computers, desktops, servers, high-power LEDs and other precision instruments. It is not cheap, but our previous test proved that it is indeed the leader among commercially available TIM products: the heat dissipation of X23-7762 was significantly better than that of the other tested traditional products. As shown in Fig.4, with X23-7762, the CPU operating temperature is basically maintained at 68 °C. When LMTG is used under the same test conditions, the temperature of the CPU stabilizes at approximately 66 °C, which is 2 °C lower than the temperature achieved with X23-7762. Meanwhile, the maximum operating temperatures achieved with ALTG and GLTG fluctuate in the vicinity of 64 °C, indicating that the heat dissipation of these high-κ particle mixtures is better than that of either the conventional thermal grease or LMTG. Because AlN powder is simple to obtain and cheaper than graphene, its advantages for cooling purposes are more obvious.

The temperatures at all points on the X1 carbon were investigated by means of two-dimensional infrared thermal imaging, as shown in Fig.5. The upper right area of the keyboard, just above the CPU, shows a bright red color indicating the highest temperature, whereas the gradually darkening color elsewhere reflects the drop in the surrounding temperature (°F). The relative effectiveness of heat dissipation could be clearly seen from the relative degrees of shading and highlighting: ALTG ≈ GLTG > LMTG > X23-7762.

2.4 Thermal mechanism

PDMS is a kind of polymer with a κ value that is generally less than 0.2 W/m·K. After the addition of thermally conductive fillers, the κ of the fillers and their dispersion in the matrix significantly affect the performance of the resulting thermal grease[19]. The thermal conductance of metal fillers mainly depends on an electronic mechanism due to the presence of a large number of electrons, whereas that of metal oxides and non-metallic materials mainly relies on phonons. When the amount of fillers is low, the particles dispersed in the PDMS are isolated from each other and thus have little effect on improving the thermal conductivity of the grease. Only when the amount of thermal fillers reaches the critical volume will the particles be in sufficient contact with each other to form effective thermal networks, and thus significantly improve the thermal conductivity.

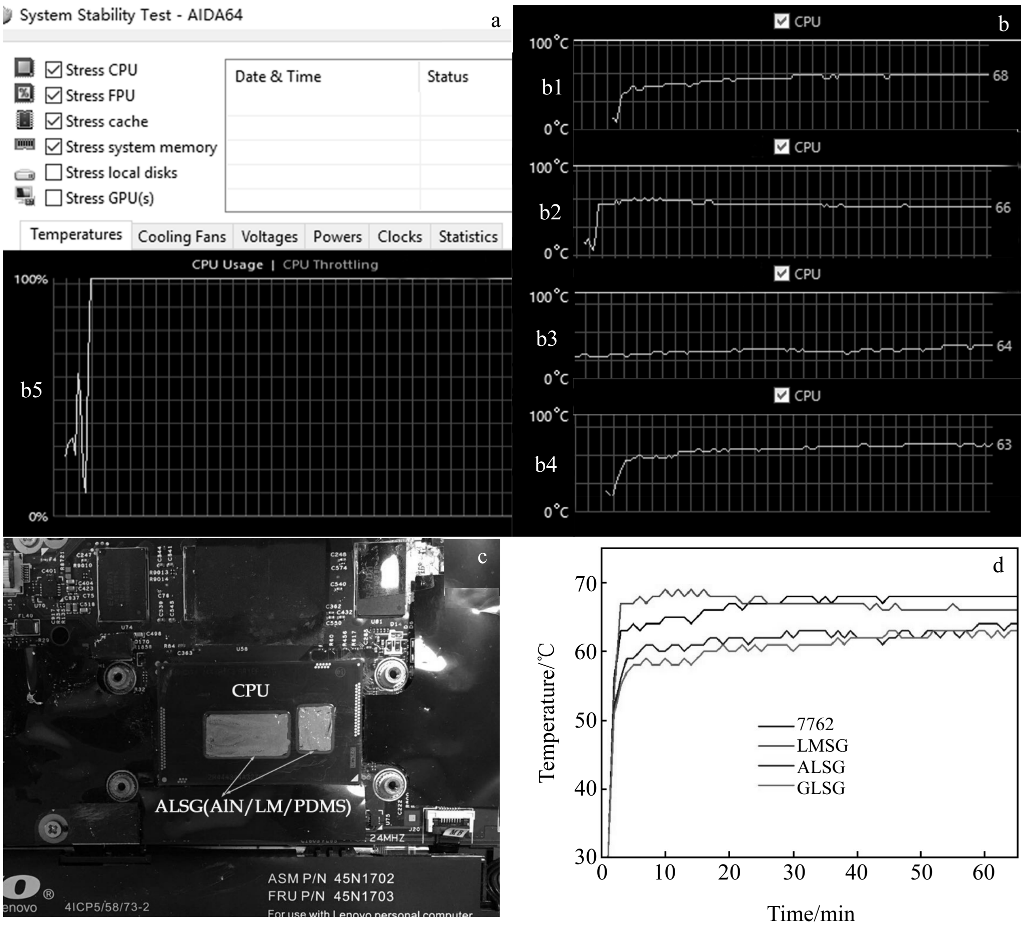

Fig.4 AIDA64 test interface (a), liquid metal silicone grease coating interface (c), and actual test data (d): (b1) 7762 temperature curve, (b2) LMTG temperature curve, (b3) ALTG temperature curve, (b4) GLTG temperature curve, and (b5) CPU loading rate

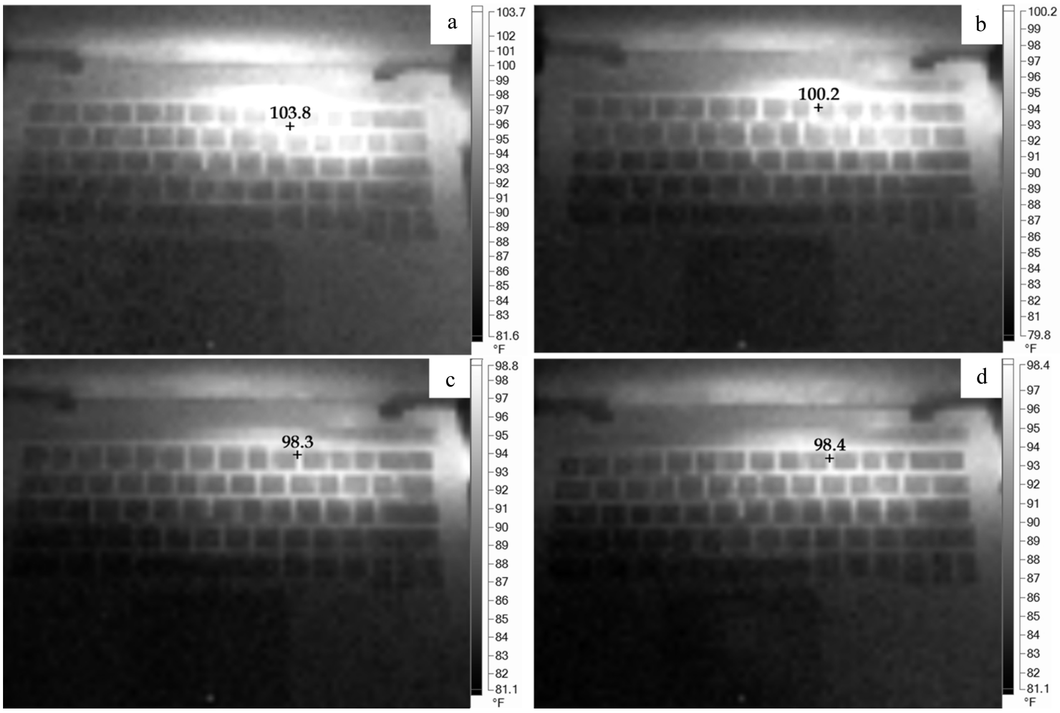

Fig.5 Infrared thermal images of the X1 carbon keyboard using X23-7762 (a), LMTG (b), ALTG (c) and GLTG (d) as TIMs

Liquid metal droplets will be uniformly dispersed in a PDMS matrix when they are mixed together to form a new TIM. A higher filler content leads to an increase in the concentration of liquid metal droplets. If they successfully form contacts with each other, their high electron conductivity will increase the thermal conductivity of the resulting material and reduce its resistivity[20]. Compared with a TIM consisting of liquid metal alone, this design is clearly more feasible because the viscosity and oxidation behavior of a pure liquid metal would pose great risk to a cooling system. However, the fluidity of LMTG is also too high for practical application, and the risk of liquid metal precipitation still exists[21].

Small liquid metal droplets in a saturated binary mixture (LMTG) tend to aggregate together to form large liquid metal droplets. Heat conduction paths are always formed through point contacts, and contact voids can easily remain. Thus, LMTG shows the potential for the formation of more heat flow paths. Upon the addition of AlN particles, with a small particle size and a high κ value, to produce ALTG, the AlN particles can fill the PDMS voids and expel the air at the convexities at an interface between electronic components. Graphene sheets act similarly, and heat paths form between the lamellae and the liquid metal help to achieve this synergistic effect. AlN and graphene can not only improve the thermal vibration of the internal lattice of a thermal grease and the mutual interactions among particles but also enable the formation of more heat paths, reducing R between the thermal grease and electronic components. With the help of this synergistic effect, ALTG and GLTG perform better than LMTG in terms of κ and R and in actual testing. Simultaneously, ALTG exhibits a viscosity consistent with market requirements, similar to that of successful commercial products, effectively reducing the risk of overflow.

3 Conclusions

1) We have synthesized a new type of TIM by combining a liquid metal/PDMS composite with highly thermally conductive AlN particles.

2)The resulting material, ALTG, exhibits the unique advantages of both a high thermal conductivity and a suitable viscosity for application. AlN particles are amenable to dispersion in thermal grease and facilitate the formation of a thermal conduction network. They are also helpful for reducing the contact thermal resistance between the TIM and device interfaces. The thermal conductivity and contact thermal resistance of ALTG were found to be 5.014 W/m·K and 15 mm^2·K/W, respectively, representing improvements of 5% and 20% compared with samples without AlN powder. This newly prepared ternary TIM shows reduced fluidity compared with pure liquid metal, thereby effectively reducing the risk of spillage.

3) Actual tests on CPU, including the commercially available silicone grease X23-7762, LMTG, GLTG and ALTG, show that ALTG has the advantages of good heat dissipation together with low cost and good practicality. Thus, ALTG is expected to be a safer and suitable TIM for cooling solutions.

References

1 Zhang K, Chai Y, Yuen M M F *et al*. *Nanotechnology*[J], 2008, 19(21): 215 706
2 Lee Y T, Shanmugan S, Mutharasu D. *Applied Physics A*[J], 2014, 114(4): 1145
3 Wang Qian, Gao Wei, Xie Zemin. *Journal of Applied Polymer Science*[J], 2003, 89(9): 2397
4 Cola B A. *Electronics Cooling*[J], 2010, 16(1): 10
5 Im Hyungu, Kim Jooheon. *Carbon*[J], 2012, 50(15): 5429
6 Zhu B L, Ma J, Yung K C *et al*. *Journal of Applied Polymer Science*[J], 2010, 118(5): 2754
7 Zhang Qin, Liu Jing. *Nano Energy*[J], 2013, 2(5): 863
8 Martin Y, Kessel T V. *International Microelectronics and Packaging Society*[J], 2007, 10: 1213
9 Gwinn J P, Webb R L. *Microelectronics Journal*[J], 2003, 34(3): 215
10 Kouraytem N, Li E Q, Thoroddsen S T. *Physical Review E*[J], 2016, 93: 063 108
11 Mei Shengfu, Gao Yunxia, Deng Zhongshan *et al*. *Journal of Electronic Packaging*[J], 2014, 136(1): 011 009
12 Andrew Fassler, Carmel Majidi. *Advanced Materials*[J], 2015, 27: 1928
13 Regan M J, Tostmann H, Pershan P S *et al*. *Physical Review B*[J], 1997, 55: 10 786
14 Sui Yanwei(隋艳伟), Feng Kun(冯 坤), Cheng Cheng(程 成) *et al*. *Rare Metal Materials and Engineering*(稀有金属材料与工程)[J], 2016, 45(12): 3062
15 Callaghan P W, Probert S D. *Journal of Mechanical Engineering Science*[J], 1974, 16(1): 41
16 Meisam Asadi, Amin A. *International Communications in Heat and Mass Transfer*[J], 2016, 76: 41
17 Sabuj M, Ndy Ekere, Chris Best *et al*. *Applied Thermal Engineering*[J], 2011, 31: 355
18 Lin Yiliang, Cooper Christopher, Wang Meng *et al*. *Small*[J], 2015, 11: 6397
19 Yahachi Saito, Masatomo Maida. *The Journal of Physical Chemistry A*[J], 1999, 103(10): 1291
20 Li L, Chung D D L. *Journal of Electronic Materials*[J], 1994, 23(6): 557
21 Chandan K Roy, Sushil Bhavnani, Michael C *et al*. *Applied Thermal Engineering*[J], 2016, 99: 72

AlN 掺杂的镓基液态金属硅脂在电子器件散热上的应用

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摘 要：为了增强界面传热效果，将镓基液态金属（$Ga_{68.5}In_{21.5}Sn_{10}$）及氮化铝作为导热填料填充到甲基硅油中制备了一种新型复合的热界面材料，并利用扫描电子显微镜（SEM）和能谱仪（EDS）检测材料的微观结构和化学成分以研究其导热原理。合成的 AlN 掺杂的镓基液态金属硅脂导热率可达 5.014 W/m·K，分别高于液态金属/甲基硅油二元复合材料和现售高端的导热硅脂产品（x-23-7762）约 5%和 20%。同时，接触热阻减少了约 20%和 50%，粘度保持在适当的范围内降低了使用过程中的溢出风险。CPU 的实测结果表明新合成的 AlN 掺杂的镓基液态金属硅脂可以显著降低笔记本核心的工作温度，分析其导热机理后提出传热过程的协同效应原理。实验结果表明该产品是一种理想的导热界面材料且具有广泛的应用前景。

关键词：镓基液态金属；氮化铝；导热硅脂；导热性能

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