

Improving the Thermal Performance of Liquid Metal Thermal Interface Materials: The Role of Intermetallic Compounds at the Gallium/Copper Interface

Xudong Zhang, Yuxia Dong, Yanzheng Du, Lei Yang, Weigang Ma, and Bingyang Cao*

Room-temperature liquid metal has been widely used in electronic packaging due to its high thermal conductivity, but its thermal performance is strongly impeded by the dominated thermal boundary resistance between liquid metal and solid material. Here, first an order-of-magnitude reduction of thermal boundary resistance (from 1.11×10^{-7} (m²·K)/W to 6.94×10^{-9} (m²·K)/W) is reported by self-synthesizing the intermetallic compound at the liquid gallium/solid copper interface. This significant thermal transport improvement is attributed to the conversion of heat carriers from phonons to electrons, and bonding force from van der Waals force to metallic bond, which is thoroughly analyzed by the microscopic phonon and electron diffuse mismatch models, complemented by molecular dynamic simulations. Chip application demonstrates that brushing liquid metal assisted by the intermetallic compound can surprisingly obtain the equivalent interfacial temperature difference (10.2 °C) to that of InSn solder welding (8.3 °C), which is much smaller than that of the conventional oxidation method (30.1 °C). This study provides a comprehensive understanding of electron/phonon transport at Ga/Cu interfaces and facilitates the giant thermal transport enhancement of liquid metal thermal interface material.

1. Introduction

Interface acts as a devil for heat transfer, and how to reduce the contact thermal resistance between two solid surfaces is a typical problem in electronic packaging.^[1–3] A common method is to brush a thermal grease on the interface, which serves to fill micro voids.^[4–6] However, the simple brushing method is far less effective in heat transfer than the welding method.^[7,8] Nowadays, with

X. Zhang, Y. Dong, Y. Du, L. Yang, W. Ma, B. Cao

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education

Department of Engineering Mechanics Tsinghua University Beijing 100084, China E-mail: caoby@tsinghua.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/admi.202500041

DOI: 10.1002/admi.202500041

the miniaturization of transistor size and the increase of packaging density, the heat generation of chips has reached an unprecedented level, and the heat generation of gallium nitride GaN and gallium oxide Ga2O3 gates has even exceeded 10 kW cm⁻².^[9,10] The traditional direct brushing method is unable to cope with such a large heat flux, and welding method will result in processing complexity and low operation efficiency. Therefore, it is challenging but highly desirable to find a new thermal interface material (TIM) with low contact thermal resistance R_c and high processing efficiency, which is to say that the ultimate pursuit of TIM is to realize equivalent thermal performance of solder welding by a fast brushing method.^[11]

Liquid metal gallium and its alloys have emerged as high performance TIMs.^[12] The intrinsic high thermal conductivity and favorable hydraulic characteristics of liquid metal make it

possess the potential of ultralow R_c and large brushing efficiency.^[13] However, physical brushing of liquid metal still has a far worse thermal performance than solder welding. The fundamental reason lies in the differences in bonding force^[14,15] and heat carriers^[16,17] across interfaces. Typically, the metal bond formed at the welding interface is much stronger than the van der Waals force at the brushing interface, and the electron heat transport at the metal interface is more effective than phonon heat transport at the brushing interface.^[18-20] Previous reports are mainly devoted to the improvement of thermal conductivity of liquid metal TIM by adding solid fillers (diamond,^[21] tungsten,^[22] copper,^[23] graphene^[24] and carbon nanotube^[25,26]) and constructing percolation network.^[27] However, as we analyzed (Note S1, Supporting Information), increasing thermal conductivity has a limited contribution to reducing R_c , while the main obstacle of liquid metal TIM is the large thermal boundary resistance $R_{\rm b}$ between liquid metal and solid material, which is about 60–90% of R_c , (Figure S1, Supporting Information).

In air, the gallium droplet is almost spherical on the copper surface,^[28,29] and poor wettability makes it difficult for gallium to enter the nano/microvoids, thus resulting in a large $R_{\rm b}$.^[30] The traditional interface treatment method is to oxidize the liquid metal to improve interface adhesion,^[31,32] but the treated

^{© 2025} The Author(s). Advanced Materials Interfaces published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.







Figure 1. Improvement of interfacial thermal transport across liquid gallium/copper heterointerfaces by self- synthesizing CuGa₂. a) Chemical treatment process; b) SEM image of the CuGa₂; c) Contact angle; d) Wettability characteristic; e) Thermal boundary resistance; f) Contact thermal resistance; g) Microscopic heat transfer mechanism.

interface, incorporated with gallium oxide, is still determined by the van der Waals force and there is a type mismatch of heat carriers between gallium oxide (phonons) and gallium/solid metals (electrons). As a result, brushing liquid metal with partial oxidation method does not achieve a significant thermal conduction enhancement. Recently, it has been found that the wettability between liquid metals and solid metals can be greatly improved by the formation of intermetallic compound at the interface through chemical processes.^[33–35] We speculate that this interface treatment method will simultaneously improve the interfacial heat transfer. However, there is no research on the interface thermal characteristics of liquid gallium/solid metal assisted by intermetallic compound, especially from the perspective of micro/nanoscale theoretical analysis and experimental measurement of interfacial heat transfer.

Here, we report an order-of-magnitude reduction of thermal boundary resistance and contact thermal resistance, by self-synthesizing the intermetallic compound at the liquid gallium/solid copper interface, experimentally measured by timedomain thermoreflectance (TDTR) and laser flash apparatus (LFA). This significant enhancement of interfacial thermal transport is due to the facilitated electron transport and strong interfacial bonding force at gallium/copper interface. By converting the interface from Ga/Ga₂O₃/Cu to Ga/CuGa₂/Cu, the thermal boundary resistance is reduced from 1.11×10^{-7} (m²·K)/W to 6.94×10^{-9} (m²·K)/W, the contact angle decreases from 145° to 41°, and the bonding force increases from 128 to 1241 mN m⁻². Chip application shows that when the heat flux is 200 W cm⁻², the interfacial temperature difference between the chip and the heat sink can reach 10.2 °C by this method, which is close to that of solder welding (8.3 °C) and much smaller than that of conventional oxidation method (30.1 °C).

2. Results

2.1. Interface Preparation and Characterization

The intermetallic compound was synthesized via an intermetallic wetting mechanism,^[36–39] which has been applied in some investigations about room-temperature liquid metal. In our study, gallium and copper were selected as liquid metal and solid material, respectively, and hydrochloric acid solution was used as the trigger. The preparation process of Ga/CuGa₂/Cu is shown in **Figure 1a**. First, the gallium was dropped on the copper, which was immersed in 1 mol L⁻¹ HCl solution. When the gallium came into contact with the copper, it suddenly collapsed



and extended to the copper. After 1 min, a new material was self-generated at the Ga/Cu interface, and it was determined as CuGa₂ by Scanning Electron Microscope (Figure 1b). CuGa₂ is a stable intermetallic compound. Its stable chemical structure endows it with excellent resistance to long-term environmental influences. During Ga diffusion into Cu, an interface structure of Ga/CuGa₂/Cu₉Ga₄/Cu evolves due to the Cu/Ga atomic ratio gradient. Given that the CuGa₂ layer exhibits a significantly greater thickness compared to the ultrathin Cu₉Ga₄ phase,^[40-42] both phases were pragmatically lumped together as CuGa₂ in our sequential compositional analysis. Figure 1c shows the spreading process. The gallium quickly spread from a spherical shape to a plane and adhered tightly to the copper. After the gallium was siphoned off, a layer of gray material remained on the surface of copper, which was copper-gallium alloy. Thus, by using the HCl solution, it is easy to self-synthesize a thin layer of CuGa2 at room temperature and to transform the conventional Ga/Ga₂O₃/Cu structure into Ga/CuGa₂/Cu structure. Such composition transformation results in a decrease in the contact angle from 145° to 41° (Figure 1d). What is worth to say that the contact angle of 145° was measured in the presence of an oxide film, not the real contact angle.^[43]

R_b of the Ga/Cu interface was experimentally measured by TDTR, a micro/nanoscale non-contact measurement technique,^[44] which were 1.11×10^{-7} (m²·K)/W and 6.94×10^{-9} $(m^2 \cdot K)/W$ before and after treating the copper with HCl solution, respectively (Figure 1e). TDTR measurement confirmed that the interface thermal transport at the Ga/Cu interface was enhanced almost sixteen times by inverting the Ga/Ga₂O₃/Cu into the Ga/CuGa2/Cu. This was the first measurement of thermal boundary resistance at the micro/nanoscale. R_c was measured by the laser flash apparatus (Note S3, Supporting Information), which were 0.188 (cm²·K)/W and 0.0126 (cm²·K)/W before and after treating the copper with HCl solution, respectively (Figure 1f). The contact thermal resistance was reduced by 90% through converting Ga/Ga₂O₃/Cu composition to Ga/CuGa₂/Cu composition. This reduction is attributed to the reduction of thermal boundary resistance, in which $R_{\rm b}$ of Ga/CuGa₂/Cu is just 5% of R_c , while the R_b of Ga/Ga₂O₃/Cu is 85% of R_c .

Figure 1g presents the microscopic interfacial heat transfer at Ga/CuGa₂/Cu structure and Ga/Ga₂O₃/Cu structure. The color highlights the temperature distribution contrast between the CuGa₂ and Ga₂O₃ interfaces under same heat flux, and the temperature decrease with the color form red to dark blue. The heat flux was applied at the bottom surface, and the bottom temperatures were also same. Specifically, the reduced interfacial thermal resistance at the CuGa₂ interface leads to a smaller temperature gradient across the material compared to the Ga_2O_3 interface($(T_1$ - T_2 < (T_1 - T_3)), resulting in the different temperature at the top surface $(T_2 > T_3)$. From a microscopic perspective, the heat transfer enhancement is due to the transition of heat carriers transport from phonon dominated (Ga/Ga2O3/Cu) to electron dominated (Ga/CuGa₂/Cu). The heat transfer at Ga/CuGa₂/Cu is through real electron transport across interface, while the heat transfer at Ga/Ga₂O₃/Cu is the combined effect of the interaction between electrons (Cu) and phonons (Ga2O3), as well as the phonon transport (Ga_2O_3) . Usually, the thermal boundary resistance dominated by electron is smaller than that of dominated by phonon.^[45] In addition, from the perspective of bonding force, The CuGa₂

alloy is bonded to copper and gallium through metallic bonds, while Ga_2O_3 is bonded to metal through van der Waals forces. The stronger the bonding force, the more favorable it is for the transport of electrons and phonons.^[46]

2.2. Interfacial Thermal Conductance

Since liquid metal is an opaque fluid, traditional TDTR measurement for the transparent liquid is not suitable for liquid metal. Here, we designed new sample structures and testing procedures (Note S4, Supporting Information). Using 500 µm transparent sapphire as the substrate, 80 nm aluminum, 5 nm nickel, and 100 nm copper were deposited in sequence to form a solid sample A (Figure 2a). Aluminum was the sensing layer whose surface reflectivity varies linearly with temperature. By obtaining the laser reflectivity of the aluminum surface, the temperature can be obtained. Nickel was a transitional layer that increases the adhesion between copper and aluminum. The liquid metal was placed in a cubic container, and then the copper side of the sample A was in contact with liquid metal. The laser was injected from the direction of the transparent sapphire substrate (Figure 2b). For measuring the thermal boundary resistance assisted by intermetallic compound, we needed to pre-treat the copper with HCl solution (Figure 2c). Sample B, consisting sapphire and aluminum, was first measured to pre-determine some thermophysical parameters (Figure 2d). The thermal conductivity of sapphire and the thermal boundary resistance of the Al/SiO₂ were measured to be 1.39 W/(m·K) and 5.56 \times 10⁻⁹ (m²·K)/W, respectively (Figure 2e). Figure 2f,g shows the raw data before and after treating with HCl solution. The thermal boundary resistances of the Ga/Cu interface were fitted to be 1.11×10^{-7} (m²·K)/W and 6.94×10^{-9} $(m^2 \cdot K)/W$, respectively.

The thermal boundary resistances were theoretically calculated below. For Ga/CuGa₂/Cu interface, the electron diffusivemismatch model (DMM) was used.^[47,48] The thermal boundary resistance was equal to the thermal resistance of the Ga/CuGa₂ interface plus that of CuGa2/Cu interface, and the thermal resistance introduced by 100 nm CuGa₂ layer was negligible (Note S5, Supporting Information). $R_{Ga/CuGa2}$ and $R_{CuGa2/Cu}$ were then calculated to be $2.7 \times 10^{-10} \text{ (m}^2 \cdot \text{K})/\text{W}$ and $2.3 \times 10^{-10} \text{ (m}^2 \cdot \text{K})/\text{W}$, respectively. The thermal boundary resistance of Ga/CuGa2/Cu was calculated as 5.0×10^{-10} (m²·K)/W, as exhibited in Figure 2h). For Ga/Ga₂O₃/Cu interface, the thermal boundary resistance can be estimated by the sum of thermal boundary resistance across the Ga/Ga₂O₃ and the Ga₂O₃/Cu interface, as well as the intrinsic thermal resistance of Ga₂O₃ interlayer (Note S6, Supporting Information). Remarkably, the thermal boundary resistances of Ga/Ga₂O₃ interface and Ga₂O₃/Cu interface were theoretically calculated by the Landauer formula combined with phonon DMM.^[49-51] Since the orientation of the interface was not available, the thermal boundary resistance was averaged over different interfacial orientations. Notably, the intrinsic thermal resistance of the Ga2O3 interlayer was calculated from the effective thermal conductivity of β -Ga₂O₃.^[52] In the almaBTE package, the effective thermal conductivity was predicted by solving the phonon Boltzmann transport equation (BTE), in conjunction with a suppression function to account for the additional phonon scattering induced by the film boundaries.^[53] The calculated thermal boundary resistances of Cu/Ga2O3, and Ga/Ga2O3 were

ADVANCED

www.advmatinterfaces.de

ADVANCED SCIENCE NEWS ______ www.advancedsciencenews.com

> (a) Sample A (b) Pump (d) **Untreated Sample A** Sample B Probe Ga SiO₂ Pump Probe (c) **HCl treated Sample A** SiO, Probe 1 mol/L HCl G Sample A (e) Experimental data Best fitting Best fitting (g) Best fitting $R_{\rm h} \pm 20\%$ 1.4 $R_{\star}\pm 20\%$ -Vin/Vout Ħ Ħ -V'in/V Untreated Sample B HCl treated 1.0 $k_{ei} = 1.39 \text{ W/(m \cdot K)}$ Sample A Sample A $R_{\rm h\,Si/Al} = 5.56 \times 10^{-9} \,({\rm m}^2 \cdot {\rm K})/{\rm W}$ $R_{b,Ga/Cu} = 1.11 \times 10^{-7} (m^2 \cdot K)/W$ $=6.94 \times 10^{-9} (m^2 \cdot K)/W$ 0.5∟ 200 200 200 400 600 1000 2000 4000 400 600 1000 400 600 1000 2000 2000 4000 4000 Delay time (ps) Delay time (ps) Delay time (ps) (j)¹²⁰ (h)^{0.6} 12 (i) 0.5 10.10 0.5 10 $R_{\rm b} \times 10^{-9} / (({\rm m}^2 \cdot {\rm K})/{\rm W})$ R_h×10⁻⁹/((m²·K)/W) /(m²·K)/W 0.4 0.3 0.27 20 0.23 0.2 $\times 10^{-9}$ 4 2.17 1 96 æ 10 0 1 6.94 0.5 0.0 Ga/CuGa₂ Cu/CuGa₂ Ga/CuGa₂/Cu Ga/Ga2O3 Cu/Ga2O3 Ga₂O₃ Ga/Ga₂O₃/Cu Experimental datas Simulation datas

Figure 2. Experimental test and Theoretical analysis of R_b . a) Sample A; b) Test procedure of untreated sample A; c) Test procedure of HCl treated sample A; d) Structure and test of Sample B; e) Raw data of sample B; f) Raw data of untreated sample A; g) Raw data of HCl treated sample A; h) Theoretical thermal boundary resistance of Ga/CuGa₂/Cu; i) Theoretical thermal boundary resistance of Ga/CuGa₂/Cu; i) Theoretical thermal boundary resistances.

 $1.96\times 10^{-9}~(m^2\cdot K)/W$, and $5.95\times 10^{-9}~(m^2\cdot K)/W$, respectively. The thermal boundary resistance was calculated as $1.01\times 10^{-8}~(m^2\cdot K)/W$, as shown in Figure 2i.

Based on the above theoretical analysis, it can be concluded that the electron-dominated $Ga/CuGa_2/Cu$ structure has a smaller thermal boundary resistance than the phonondominated $Ga/Ga_2O_3/Cu$ structure. The decreasing percentage of theoretical calculation is consistent with that of experimental measurement. However, as shown in Figure 2j, the experimental values of thermal boundary resistance are larger than theoretical values. This is because theoretical values are actually for the ideal interfaces, and do not consider the various defects at the practical interface and the interlayer are not considered. In addition, the DMM predicted transmittance is only frequency dependent, which leads to an overestimation of the contribution of phonons with large incident angles. As a result, the predicted thermal boundary resistances are smaller than the experimental values.

2.3. Interfacial Hydrodynamic Characteristics

Surface tension γ is used to evaluate the physical property of gallium itself, which is about 707 mN m⁻¹. And adhesion work *W* is used to evaluate the interaction between liquid metal and copper. The theoretical adhesion work can be estimated by the following Equation $(1)^{[54]}$:

 $W = \gamma \cdot (1 + \cos \theta) \tag{1}$

where θ refers to the contact angle, and γ represents the surface tension of gallium. To determine the adhesion work for Ga/Cu interface in the presence of intermediate layer of CuGa₂ and Ga_2O_2 , the force balance method was adopted, as shown in Figure 3a. The experiment was conducted in a commercial solderability tester. As the copper strip slowly inserting into gallium, the force of copper strip was balanced vertically by the pulling force from the device *F*, buoyancy force from gallium $F_{\rm b}$ and the wetting force in the vertical direction $\gamma l\cos\theta$ (Figure 3b). The pulling force evolution (Figure 3c) shows that there was a significant difference in bonding force at Ga/Cu interface before and after using HCl. By measuring F and calculating $F_{\rm b}$, $\gamma \cos\theta$ were then obtained, which is 0.326 mJ m^{-2} for Ga/CuGa₂/Cu structure. And then adhesion works were calculated as 1033 mJ m^{-2} for Ga/CuGa₂/Cu structure. More measurement principles and calculation procedures were detailed in Note S7 (Supporting Information). The theoretical adhesion work for Ga/CuGa₂/Cu structure and $Ga/Ga_2O_3/Cu$ structure was calculated by Equation (1), by using $\gamma = 707$ mN m⁻¹ and $\theta = 41^{\circ}$, 145°. The value of www.advancedsciencenews.com

SCIENCE NEWS



www.advmatinterfaces.de



Figure 3. Interfacial wetting characterization of Ga/Cu. a) Schematic diagram of the wetting force test; b) Force equilibrium of a copper bar; c) The wetting force; d) Simulated geometrical model; e)The wetting and diffusion process; f) The atom distribution; g) The atom distribution in the region of z = 3.05-3.25 nm.

Ga/CuGa₂/Cu structure was calculated to be 1241 mJ m⁻², which was close to the experimental values 1033 mJ m⁻². And that of Ga/Ga₂O₃/Cu structure was 128 mJ m⁻².

There is a criterion for judging the type of bonding force^[55]: Van der Waals physical bonding exists if the adhesion work is less than 0.2 times of the cohesive force, but chemical bonding exists if the adhesion work is greater than 0.2 times of the cohesive force, as shown in Equations (2) and (3). The cohesive force of gallium is calculated to be 1414 mJ m⁻², as calculated by Equation (4). Therefore, the interface bonding force is Van der Waals force in air, while the interface bonding force is the metallic bond after the interface with HCl treated. Consequently, assisted by metallic compound, the bonding force of Ga/Cu interface changes from van der Waals force to metallic bond, and the adhesion work is improved by almost ten times.

Vander Waals Force : $W < 0.2 \cdot W_{cohesion}$ (2)

Chemical Force or Metallic Force :
$$W > 0.2 \cdot W_{cohesion}$$
 (3)

$$W_{cohesion} = 2\gamma \tag{4}$$

To reveal the wetting mechanism at the Ga/Cu interface, a molecular dynamic (MD) simulation was conducted. The total dimensions were 14 nm \times 14 nm \times 12 nm, the dimensions of copper were 14 nm \times 14 nm \times 3 nm, and the diameter of the spherical gallium was 4 nm (Figure 3d). Modified EAM (MEAM) was used to simulate the interaction between gallium atoms,[56,57] and the MEAM potential was also used to model the interaction between copper atoms.^[58] The Lennard-Jones potential function was adopted to model the interaction between gallium and copper atoms. The Lennard-Jones potential function was controlled by two parameters: the sphere of influence σ and potential depth ε . σ was calculated by first principles to be 2.102 Å. Based on the experimental contact angle of the gallium on the copper surface, σ was obtained by fitting $\varepsilon = 0.5338$ eV. The time step of the simulation was set to 1 fs and the total simulation time was 5 ns. The surface tension calculated from molecular dynamics simulation



www.advmatinterfaces.de



Figure 4. Comparison of different TIMs. a) Morphology of different samples; b) The thermal diffusivity; c) Contact thermal resistance; d) Variation of contact thermal resistance with temperature; e) Module under test; f) The variation of ΔT with time *t*; g) The temperature of chip $T_{\rm B}$ with time *t*.

was 854 mN m $^{-1}$ (Note S8, Supporting Information), which was close to the experimental value of 707 mN m $^{-1}.^{\rm [59]}$

The hydrodynamic behavior of gallium on copper was a wetting-diffusion process (Figure 3e). Within 500 ps, the spherical gallium diffused rapidly on the copper and the wetting angle decreased from 145° to 40° and it stabilized at 40°. At the same time, gallium and copper diffused into each other at the interface, forming a Cu-Ga alloy layer. Therefore, this period was named the wetting–diffusion stage. After 500 ps, the contact angle and atom distribution remained almost unchanged (Movie S1, Supporting Information). In order to quantitatively characterize the diffusion process of copper and gallium atoms, thin slices were cut parallel to the x-y plane with a slice spacing of 0.12 nm. Figure 3f shows the variation of gallium atom ratios at different times. The thickness of the diffusion layer gradually increased with time and the rate of increase slowed down with time. It can also be seen that the gallium atoms diffused deeper into the copper. This is because the copper atoms at the far end have a strong attraction to the copper atoms at the interface, while the gallium atoms at the far end have a weaker attraction to the gallium atoms at the interface. Figure 3g shows the atom fraction in the range of z =3.05~3.25 nm, and intermetallic compound CuGa₂ was found. Moreover, the atom fraction did not change with time after 1 ns, which verifies that CuGa₂ was a stable product, as found it in Figure 1b.

2.4. Chip Applications with Different TIMs

The heat transfer properties of different TIMs were compared, including untreated liquid metal (LM), HCl treated LM, InSn solder and SnAgCu solder (Figure 4a). TIM was filled into the interface between two copper plates, forming a sandwich

SCIENCE NEWS

www.advancedsciencenews.com

structure. The thermal diffusivities of four samples were tested by LFA (Figure 4b). It can be seen that the HCl treated liquid metal has a thermal diffusivity of 80 mm² s⁻¹, which is close to that of solder welding (100 mm² s⁻¹). The thermal diffusivity of the untreated liquid metal is just 30 mm² s⁻¹. Thermal conductivities of four samples are equal to density multiplied by specific heat capacity multiplied by thermal diffusivity. Due to the relatively small weight of the TIM compared to copper, the density and specific heat capacity of the four samples can be approximately equal to that of copper. Therefore, the thermal conductivity is directly proportional to the thermal diffusivity. Notably, the contact thermal resistances of four TIMs are obtained by subtracting the thermal conduction resistance of copper from the total thermal resistance. As can be seen in Figure 4c, the contact thermal resistance of solder welding is very closed to that HCl treated liquid metal, which is about 20% that of untreated liquid metal. Thus, the brushing gallium grease assisted by metallic compound achieves the equivalent contact thermal resistance as solder welding. Moreover, it has a stable thermal performance in the range of 20-60 °C, as shown in Figure 4d.

The chip applications were conducted to present the thermal performance of TIMs (Figure 4e; Note \$9, Supporting Information). The chip was a high heat flux heat source and heat sink was a water microchannel cooler. The interface between the chip and the heat sink was filled with TIM. Thermocouple A and B were inserted into the interface to monitor the temperatures of heat sink and chip, respectively. Notably, the smaller the $\Delta T (T_{\rm B} - T_{\rm A})$, the better the performance of TIM. Figure 4f shows ΔT at different heat fluxes. When the heat flux was equal to 100 W cm⁻², the temperature differences for untreated LM, HCl treated LM and InSn welding were 15.6, 5.4, and 4.1 °C, respectively. The temperature difference of the HCl treated LM was much smaller than that of the untreated LM, which was close to that of the InSn solder welding. Even at a heat flux of 200 W cm⁻², the temperature difference for gallium with HCl treated was only 10.6 °C, which indicated the excellent thermal performance of this method. The brushing method, on the other hand, can handle a heat flux of 200 W cm⁻² and the maximum chip temperature can be kept below 71 °C, as shown in Figure 4g.

3. Discussion

In this study, the thermal boundary resistance of the liquid Ga/CuGa₂/Cu structure (1.11×10^{-7} (m²·K)/W) has an orderof-magnitude reduction compared to that of conventional liquid Ga/Ga₂O₃/Cu structure (6.94×10^{-9} (m²·K)/W) as measured by the time-domain thermoreflectance method. This giant improvement is attributed to the conversion of heat carriers from phonons to electrons, and bonding force from Van der Waals force to metallic bond. Chip application shows that at a heat flux of 200 W cm⁻², our method results in an temperature difference between the chip and the heat sink of 10.2 °C, which is close to that of InSn welding (8.3 °C) and much smaller than that of conventional oxidation method (30.1 °C).

Our work is the first to comprehensively analyze how the transition from phonon-dominated heat transfer in the $Ga/Ga_2O_3/Cu$ structure to electron dominated heat transfer in the $Ga/CuGa_2/Cu$ structure occurs. We have quantitatively demonstrated the superiority of electron based heat transfer in

reducing thermal boundary resistance through a combination of advanced theoretical models and experimental validations. This new understanding of the heat carrier conversion mechanism can serve as a guiding principle for the design of next generation thermal interface materials. It is believed that this method will play an important role in promoting the thermal performance of liquid metal TIMs and dealing with the extreme heat dissipation of chips. Such a strategy also inspires improving the wettability between liquid metals and non-metals such as diamond, graphene, boron nitride and carbon nanotubes by coating a thin metal.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 52206098, 52425601, U20A20301, 52327809, 52250273 and 82361138571), the China Postdoctoral Science Foundation (Grant No. 2021M701852), the National Key Research and Development Program of China (Grant No. 2023YFB4404104), and Beijing Natural Science Foundation (No. L233022).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

bonding strength, electron transport, liquid metal, thermal conductance, thermal interface material

Received: January 16, 2025 Revised: April 13, 2025 Published online:

- P. J. O'Brien, S. Shenogin, J. Liu, P. Chow, D. Laurencin, P. Mutin, M. Yamaguchi, P. Keblinski, G. Ramanath, *Nat. Mater.* 2013, 12, 118.
- [2] A. Giri, P. E. Hopkins, Adv. Funct. Mater. 2020, 30, 1903857.
- [3] J. Chen, X. Xu, J. Zhou, B. Li, Rev. Mod. Phys. 2022, 94, 025002.
- [4] D. D. L. Chung, Small 2022, 18, 2200693.
- [5] Y. Cui, Z. Qin, H. Wu, M. Li, Y. Hu, Nat. Commun. 2021, 12, 1284.
- [6] W. Zhou, Y. Wang, F. Kong, W. Peng, Y. Wang, M. Yuan, X. Han, X. Liu, B. Li, Energy Environ. Mater. 2024, 7, 12698.
- [7] X. Zhang, G. Yang, B. Cao, Adv. Mater. Interfaces 2022, 9, 2200078.
- [8] R. Zhang, J. Cai, Q. Wang, J. Li, Y. Hu, H. Du, L. Li, J. Electron. Packag. 2014, 136, 011012.
- [9] R. Van Erp, R. Soleimanzadeh, L. Nela, G. Kampitsis, E. Matioli, Nature 2020, 585, 211.

21967350, 0, Downloaded from https://advanced.onlinelibrary.wiley.com/doi/10.1002/admi.202500041, Wiley Online Library on [08/05/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

- [10] Y. Hua, Y. Shen, B. Cao, A. John Patrick, G. John M, W. J. Minkowycz,
- Adv. Heat Transfer. 2023, 56, 355. [11] K. Razeeb, E. Dalton, G. Cross, A. Robinson, Int. Mater. Rev. 2018, 63,
- I.
 Y. Gao, J. Liu, Appl. Phys. A-Mater. 2012, 107, 701.

ADVANCED SCIENCE NEWS ______

- [13] S. Tang, C. Tabor, K. Kalantar-Zadeh, D. Dickey, Annu. Rev. Mater. Res. 2021, 51, 381.
- [14] W. Dai, X. Ren, Q. Yan, S. Wang, M. Yang, L. Lv, J. Ying, L. Chen, P. Tao, L. Sun, C. Xue, J. Yu, C. Song, K. Nishimura, N. Jiang, C. Lin, Nano-Micro Lett. 2023, 15, 9.
- [15] H. Harikrishna, W. Ducker, S. Huxtable, Appl. Phys. Lett. 2013, 102, 251606.
- [16] P. Hopkins, Int. Scholarly Res. Not. 2013, 2013, 682586.
- [17] G. Chen, Nanoscale Energy Transport and Conversion: A Parallel Treatment of Electrons, Molecules, Phonons, and Photons, Oxford University Press, Oxfordshire UK 2005.
- [18] B. Shi, X. Tang, T. Lu, T. Nakaysma, Y. Li, J. Zhou, Mod. Phys. Lett. B 2018, 32, 1830004.
- [19] B. Gundrum, D. Cahill, R. Averback, Phys. Rev. B 2005, 72, 245426.
- [20] G. Chen, Nat. Rev. Phys. 2021, 3, 555.
- [21] C. Roy, S. Bhavnani, M. Hamilton, R. Johnson, J. Nguyen, R. Knight, D. Harris, Int. J. Heat Mass Tran. 2015, 85, 996.
- [22] W. Xing, H. Wang, S. Chen, P. Tao, W. Shang, B. Fu, C. Song, T. Deng, Adv. Eng. Mater. 2022, 24, 2101678.
- [23] H. Wang, W. Xing, S. Chen, C. Song, M. Dickey, Adv. Mater. 2021, 33, 2103104.
- [24] X. Zhang, X. Yang, Y. Zhou, W. Rao, J. Gao, Y. Ding, Q. Shu, J. Liu, Energ. Convers. Manage. 2019, 185, 248.
- [25] J. Tang, S. Lambie, N. Meftahi, A. Christofferson, J. Yang, M. Ghasemian, J. Han, F. Allioux, M. Rahim, M. Mayyas, *Nat. Nanotech*nol. **2021**, *16*, 431.
- [26] K. Wu, Z. Dou, S. Deng, D. Wu, B. Zhang, H. Yang, R. Li, C. Lei, Y. Zhang, Q. Fu, G. Yu, Nat. Nanotechnol. 2024, 20, 104.
- [27] X. Li, B. Xiao, L. Cao, F. Li, J. Yang, J. Hu, T. Cole, Y. Zhang, M. Zhang, S. Zhang, W. Li, S. Li, X. Chen, S. Tang, *Adv. Sci.* **2022**, *9*, 2105289.
- [28] J. Tang, X. Zhao, J. Li, R. Guo, Y. Zhou, J. Liu, ACS Appl. Mater. Interfaces 2017, 9, 35977.
- [29] X. Zhao, S. Xu, J. Liu, Front. Energy 2017, 11, 535.
- [30] S. Y. Tang, C. Tabor, K. Kalantar-Zadeh, D. Dickey, Annu. Rev. Mater. Res. 2021, 51, 381.
- [31] C. Wang, Y. Gong, B. Cunning, S. Lee, Q. Le, S. Joshi, O. Buyukcakir, H. Zhang, W. Seong, M. Huang, M. Wang, J. Lee, G. Kim, R. Ruoff, *Sci. Adv.* **2021**, *7*, abe3767.
- [32] D. Wang, X. Wang, W. Rao, Acc. Mater. Res. 2021, 2, 1093.

[33] X. Du, W. Wang, Z. Ding, X. Wang, Y. Qiao, S. Wei, Q. Zhu, J. Guo, J. Mater. Sci-Mater. El. 2023, 34, 1336.

4DVANCED

www.advmatinterfaces.de

- [34] Q. He, M. Qin, H. Zhang, S. Wang, W. Feng, Nano Today 2024, 59, 102549.
- [35] J. Tang, S. Lambie, N. Meftahi, A. Christofferson, J. Yang, M. Ghasemian, J. Han, F. Allioux, M. Rahim, M. Mayyas, T. Daeneke, C. McConville, K. Steenbergen, R. Kaner, S. Russo, N. Gaston, K. K. Zadeh, *Nat. Nanotechnol.* **2021**, *16*, 431.
- [36] J. H. Kim, S. Kim, H. Kim, S. Wooh, J. Cho, M. Dickey, J. H. So, H. J. Koo, Nat. Commun. 2022, 13, 4763.
- [37] J. Tang, X. Zhao, J. Li, Y. X. Zhou, J. Liu, Adv. Sci. 2017, 4, 1700024.
- [38] S. A. Idrus-Saidi, J. Tang, S. Lambie, J. Han, M. Mayyas, M. Ghasemian, F. Allioux, S. Cai, P. Koshy, P. Mostaghimi, K. Steenbergen, A. Barnard, T. Daeneke, N. Gaston, K. K. Zadeh, *Science* 2022, *378*, 1118.
- [39] Y. Cui, F. Liang, Z. Yang, S. Xu, X. Zhao, Y. Ding, Z. Lin, J. Liu, ACS Appl. Mater. Interfaces 2018, 10, 9203.
- [40] Y. Chen, C. Liu, Z. Zhou, C. Liu, J. Manuf. Processes **2022**, 84, 1310.
- [41] Z. Gao, Y. Chen, C. Wang, K. Yao, Z. Chai, H. Ma, Y. Wang, M. Huang, *Mater. Lett.* 2022, 307, 131029.
- [42] T. Gancarz, K. Berent, Mater. Lett. 2018, 227, 116.
- [43] I. Joshipura, K. Persson, V. Truong, J. Oh, M. Kong, M. Vong, C. Ni, M. Alsafatwi, D. Parekh, H. Zhao, M. Dickey, *Langmuir* **2021**, *37*, 10914.
- [44] P. Jiang, X. Qian, Y. R. Tutorial, J. Appl. Phys. 2018, 124, 161103.
- [45] B. C. Gundrum, D. G. Cahill, R. S. Averback, Phys. Rev. B 2005, 72, 245426.
- [46] Z. Tian, A. Marconnet, G. Chen, Appl. Phys. Lett. 2015, 106, 211602.
- [47] R. B. Wilson, D. G. Cahill, Phys. Rev. Lett. 2012, 108, 255901.
- [48] D. A. Saha, X. Yu, M. Jeong, M. Darwish, J. Weldon, A. Gellman, J. Malen, Phys. Rev. B 2019, 99, 115418.
- [49] Q. Song, G. Chen, Phys. Rev. B 2021, 104, 085310.
- [50] H. Yang, B. Cao, J. Appl. Phys. 2023, 134, 155302.
- [51] E. T. Swartz, R. O. Pohl, Rev. Mod. Phys. 1989, 61, 605.
- [52] L. Yang, B. Cao, J. Phys. D Appl. Phys. 2021, 54, 505302.
- [53] J. Carrete, B. Vermeersch, A. Katre, A. Roekeghem, T. Wang, G. Madsen, M. N. almaBTE, Comput. Phys. Commun. 2017, 220, 351.
- [54] D. E. Packham, Int. J. Adhes. Adhes. 1996, 16, 121.
- [55] P. G. D. Gennes, Rev. Mod. Phys. 1985, 57, 827.
- [56] M. Baskes, S. Chen, F. Cherne, Phys. Rev. B 2002, 66, 104107.
- [57] M. I. Baskes, Phys. Rev. B **1992**, 46, 2727.
- [58] S. Plimpton, J. Comput. Phys. 1995, 117, 1.
- [59] H. Heinz, R. A. Vaia, B. L. Farmer, R. R. Naik, J. Phys. Chem. C 2008, 112, 17281.