Supplementary Material for

The Enhancement of Heat Conduction Across the Metal/Graphite Interface Treated with Focused Ion Beam

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The fitting details of time-domain thermoreflectance technique

The fitting process of time-domain thermoreflectance (TDTR) technique is similar to the previous literature [1]. When fitting the measured phase decay curves with a thermal model to obtain the interfacial thermal conductance between Al and graphite, there are three unknown fitting parameters, namely the in-plane thermal conductivity k_{in} of the graphite sheet, the out-plane thermal conductivity k_{out} of the graphite sheet, the out-plane thermal conductivity k_{out} of the graphite sheet and the interfacial thermal conductance $G_{Al/graphite}$ between Al and graphite. These three parameters are set as unknown fitting parameters, because their values changes with different thickness of graphite sheets or different treatment conditions of the interfaces. The other unknown parameters are obtained from the literatures due to their constant values during the measurements, such as the thermal conductivity of Al, the heat capacity of Al and the heat capacity of graphite. The size effects on the Al film are out of consideration, because the thickness of Al film is controlled to be 70 nm for each sample by magnetron sputtering method during all the measurements. And it was reported that the Al film has a constant thermal conductivity for its thickness larger than

50 nm [2]. However, the size effects on the graphite sheet are taken into account, since the thickness of graphite sheet ranges from 40 nm and 730 nm for different samples in the measurement. By fitting the thickness-dependent thermal conductivity of the graphite sheet with the thermal model [3], the results can be shown in Fig. S1, which are consistent with the previous report [1, 4].



Figure S1. the measured out-plane thermal conductivity of graphite sheet as functions of thickness. The red hollow squares denote the experimental data from Hang *et al.* [1], while the blue hollow circles denote the experimental data from Qiang *et al.* [4].

The error bars in Fig. 3 of the main text come from the fitting error according to the sensitivity analysis as shown in Fig. S2. The phase sensitivity to a parameter α is defined as follows, which is similar to that of Bryan *et al.* [5]:

$$S_{\phi,\alpha} = \frac{dln\phi}{dln\alpha} \tag{S1}$$

Where the parameter α can represents k_{in} , k_{out} or $G_{Al/graphite}$. For the heterostructure containing Al and pristine graphite as shown in Fig. S2(a), the maximum of the phase sensitivity to changes in the interfacial thermal conductance $G_{Al/graphite}$ equals to 0.1 at delay times near 100 ps. That means, a 10% increase in $G_{Al/graphite}$ produces a 1% increase in the phase signal. Meanwhile, the maximum of the phase sensitivity to

changes in the in-plane thermal conductivity k_{in} of the pristine graphite sheet equals to 0.5 at delay times near 100 ps. In other words, a 2% decrease in k_{in} produces a 1% decrease in the phase signal. Considering the deviations of three unknown fitting parameters k_{in} , k_{out} or $G_{Al/graphite}$ can lead to the fluctuation of the phase, when k_{in} , k_{out} or $G_{Al/graphite}$ vary within a specific range simultaneously, it is possible to keep the phase nearly unchanged. This phenomenon results in the fitting error. In order to estimate the fitting error, we vary the fitting values of k_{in} , k_{out} and $G_{Al/graphite}$ to observe whether the measured phase decay curves can still fit the thermal model with excellent quality. If the measured phase decay curves fit the thermal model very well, we record the fitting values of k_{in} , k_{out} and $G_{Al/graphite}$. Otherwise, if the discrepancy in the measured phase decay curves and the thermal model makes this fitting of poor quality, the fitting values of k_{in} , k_{out} and $G_{Al/graphite}$ are out of counting. Finally, the error bars are obtained from the twofold standard deviations of the fitting values with excellent fitting quality. This method is similar to that from the previous literature [1]. In addition, the fitting error is inversely proportional to the phase sensitivity. As can be seen in Fig. S2(b), the interfacial thermal conductance between Al and milled graphite $G_{Al/graphite}$ has a low phase sensitivity, due to its high interfacial thermal conductance compared to the low thermal conductivity of milled graphite. That is the reason why the interfacial thermal conductance between Al and milled graphite has a long error bar as shown in Fig. 3 of the main text.



Figure S2. the phase sensitivity as functions of delay time for (a) the heterostructure containing Al

and pristine graphite, (b) the heterostructure containing Al and milled graphite.

The change of the graphite surface roughness after treated with the focused ion beam

The atomic force microscopy (AFM) topographic images of pristine graphite and the milled graphite is shown in Fig. S3. The surface roughness of graphite at the pristine portion and milled portion is measured to be at 233 pm and 192 pm, respectively, which shows extremely slight difference. It is reported that for the focused ion beam (FIB) milling by surface scanning, the puddles-like surface texture can be described by the square of the cosine function [6], making the surface roughness range from 3 to 10 nm [7]. However, in our work, the graphite is milled by the focused ion beam with fixed position as shown in Fig. S3. This is the reason why the surface roughness of graphite at the milled portion in our work is less than the values of literature [7]. Besides, other experiment reports that the surface roughness of milled silicon caused by ion beam can be controlled below 1 nm for the exposure time < 2 min [8], in which the value is similar to that of the milled graphite in our work. Moreover, it is investigated that FIB milling only induce the surface destruction with atom-scale surface roughness using transmission electron microscope [9], consistent with the AFM results shown in Fig. S3.



Figure S3. (a) The optical microscope image of graphite after FIB milling. (b) The atomic force microscopy topographic images of the pristine graphite. (c) The atomic force microscopy topographic images of the milled graphite. The resolution along x and y directions is 1 nm, and along z direction is 0.1 nm. The milled portion of graphite is prepared under the same condition as case 1 in the main text.

The Fermi level difference between milled graphite and pristine graphite under different exposure time

The Fermi level differences between FIB-treated graphite and pristine graphite under different exposure time are measured by the scanning Kelvin probe microscopy (SKPM), which are nearly unchanged as shown in Fig. S4.



Figure S4. SKPM measured Fermi level difference between FIB-treated graphite and pristine graphite under different exposure time.

Negligible electron contributions to the interfacial thermal conductance

In order to evaluate the electron contributions to the interfacial thermal conductance between Al and non-defected graphite/defected graphite, QuantumWise Atomistix Toolkit (ATK) [10] combining the density functional theory (DFT) and the nonequilibrium Green's function (NEGF) methods is used to calculate the electron transmission. The exchange correlation interaction is treated with local density approximation (LDA) [11]. A $5 \times 5 \times 100$ Monkhorst-Pack *k*-point sampling is employed to calculate the Brillouin zone integration. As seen from Fig. S5, the electron transmission of the heterostructure containing defected graphite has been enhanced due to stronger binding energy and smaller equilibrium separations as mentioned in the main text. However, both the electron transmissions of two heterostructures equal to zero at Fermi level, indicating that negligible electrons with high mobility at Fermi surface have the ability to transfer across the interface between Al and graphite [12]. Furthermore, in order to estimate the electron contributions to the interfacial thermal conductance, Onsager coefficients should be first calculated as follows [13]:

$$L_n(\mu,T) = \int -\frac{\partial f_F(E,\mu,T)}{\partial E} \cdot (E-\mu)^n \cdot T(E) dE$$
(S2)

Where f_F represents the Fermi distribution function, μ represents the chemical potential, and T is the electron transmission. Then, the electron contributions to thermal conductance can be expressed as follows [13]:

$$\sigma_{el} = \frac{2}{AhT} \left(L_2 - \frac{L_1^2}{L_0} \right) \tag{S3}$$

Where *A* represents the cross-sectional area of the heterostructure, and *h* represents the Planck constant. Assuming that the chemical potential μ equals to the Fermi level $\varepsilon_{\rm F}$, according to Eq. (S3). the electron contributions to the interfacial thermal conductance between Al and non-defected graphite/defected graphite are calculated to be 0.1×10^{-6} MW/m²K and 77.5×10^{-6} MW/m²K respectively. Although the enhancement of the electron contributions to the interfacial thermal conductance between Al and defected graphite has been observed, the value is still negligible compared with the increased interfacial thermal conductance, which is up to ~170 W/m²K as presented in the main text.



Figure S5. The electron transmission spectrum of the heterostructures containing Al and non-

defected graphite/defected graphite. Both heterostructures are the same as those in Fig. 5 of the main text. ϵ_F represents the Fermi level.

Nonequilibrium Green's function method

The schematic diagram of the heterostructure used in the NEGF method is shown in Fig. S6. Molecular dynamics (MD) calculations are preformed to determine the interatomic force constants (IFCs) using the Large-scale Atomic/Molecular Massively Parallel Simulator package (LAMMPS) [14]. The in-plane atomic interactions of graphite are modeled by the Tersoff potential [15] and the interlayer interactions are modeled by the Lennard-Jones (LJ) potential [16], while the atomic interactions of Al are modeled by the embedded atom method (EAM) potential [17]. The LJ potential is adopted to simulate interatomic forces between Al and C atoms at the interface as follows:

$$V(r) = 4\chi\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(S4)

Where the ε and σ represent the well-dept and equilibrium interatomic distance at null potential respectively, and χ is a dimensionless scaling factor used to adjust the interaction strength between Al and C atoms. The values of ε and σ are recommended to be set as 35 meV and 3.0135 Å based on the Lorrentz-Berthelot mixing rules [18]. However, in our work the value of ε is set as 2.80 meV to fit the experimental results of interfacial thermal conductance between pristine graphite and Al, which is consistent with the value of 2.96 meV in the LJ potential of graphite interlayer interactions [19]. Employing the IFCs calculated from MD method, the green's function G_D corresponding to the central region can be calculated as [20-22]:

$$G_D = \left[\omega^2 I - H_D - \Sigma_{LC} - \Sigma_{RC}\right]^{-1}$$
(S5)

Where ω is the phonon frequency, H_D represents the harmonic matrix of the central region. Σ_{LC} and Σ_{RC} are the self-energy matrices of the left and right contacts. With the green's function, the transmission function $\Xi(\omega)$ representing the propagation of phonons between two contacts can be calculated as [21, 22]:

$$\Xi(\omega) = \frac{1}{A} Tr(\Gamma_L G_C \Gamma_R G_C^+)$$
(S6)

Where $\Gamma_L = i(\Sigma_L - \Sigma_L^+)$, $\Gamma_R = i(\Sigma_R - \Sigma_R^+)$, and "+" denotes the conjugate transpose of the matrix. *A* represents the cross-sectional area of the heterostructure. The thermal conductance (σ) can be calculated using Landauer formula [20, 21]:

$$\sigma = \int_{0}^{\infty} \frac{\hbar\omega}{2\pi} N(\omega) \Xi(\omega) d\omega$$

$$N(\omega) = \frac{\hbar\omega}{k_{B}T^{2}} \frac{e^{\frac{\hbar\omega}{k_{B}T}}}{(e^{\frac{\hbar\omega}{k_{B}T}} - 1)^{2}}$$
(S8)

Where \hbar is the reduced Planck constant, k_B is the Boltzmann's constant, and *T* is temperature. The thermal conductance obtained from the NEGF method has units of [W/m²K]. To exclude the influence from the thermal resistance of Al and graphite at both sides of the interface, the interfacial thermal conductance between Al and graphite can be modified as [23, 24]:

$$\sigma_{Al/Graphite} = \frac{\sigma}{1 - \frac{1}{2} \left(\frac{\sigma}{\sigma_{Al}} + \frac{\sigma}{\sigma_{Graphite}} \right)}$$
(S9)

Where σ_{Al} and $\sigma_{Graphite}$ are the thermal conductance of pure Al and pure graphite, respectively. Transmittance can be related to transmission function as [23, 24]:

$$\tau_{Al \to Graphite}(\omega) = \frac{\Xi(\omega)}{\Xi_{Al}(\omega)}$$
(S10)

$$\tau_{Graphite \to Al}(\omega) = \frac{\Xi(\omega)}{\Xi_{Graphite}(\omega)}$$
(S11)

Where $\tau_{Al \to Graphite}(\omega)$ represents the transmittance from Al to graphite, while $\tau_{Graphite \to Al}(\omega)$ represents the transmittance from graphite to Al.



Figure S6. The schematic diagram of the heterostructure used in NEGF method. In the schematic diagram, the device (D) region only interacts with the left contact (LC) region and the right contact (RC) region. The left contact bulk (LCB) region only interacts with the LC region, while the right contact bulk (RCB) region only interacts with the RC region.

Effects of phonon focusing on the interfacial thermal conductance

Recently, the MD simulation results demonstrate that phonon focusing effect plays a non-negligible role in enhancing the interfacial thermal conductance consisting of graphite [25, 26] by decreasing the in-plane binding strength or increasing the crossplane binding strength of graphite, which can increase the group velocity component along the cross-plane direction. According to this mechanism of enhanced interfacial thermal conductance, it is necessary to figure out whether the defects can induce an enhancement of the interfacial thermal conductance by the same way, due to the fact

that introducing defects contributes to the reduction of the in-plane tensile elastic constants of graphite. Prior to this question, we first discuss how the defects affect the in-plane thermal conductivity of the graphite. In our work, the elastic constants of graphite are calculated using the DFT methods with different defect concentrations of 0%, 6.25% and 12.5% respectively. The values of the elastic constants C_{11} and C_{33} with three different defect concentrations of graphite are showed in the inset of Fig. S7 (a). It can be seen that 6.25% defect concentrations of graphite leads to $\sim 26\%$ reduction of the intralayer interactions and $\sim 7\%$ reduction of the interlayer interactions, while 12.5% defect concentrations lead to ~52% reduction of the intralayer interactions and ~24% reduction of the interlayer interactions. It is reported that the in-plane thermal conductivity of the graphite $k_{in} \propto \chi_{in}^{1.22}$ and $k_{in} \propto \chi_{out}^{-0.04}$, while χ_{in} and χ_{out} represent the dimensionless scaling factors of the intralayer interactions and the interlayer interactions, respectively [26]. According to this literature, it can be estimated that 6.25% defect concentrations of graphite will lead to ~30% reduction of the in-plane thermal conductivity, while 12.5% defect concentrations will lead to ~59% reduction of the in-plane thermal conductivity. This estimation draws the conclusion that the defects have a great effect on the thermal transport process in graphite.

Back to the discussion of whether there is an enhanced interfacial thermal conductance induced by defects, in order to obtain the elastic constants as a function of the defect concentrations, the parabolic functions are used to fit the elastic constants of graphite with the defect concentrations of 0%, 6.25% and 12.5% (obtained by the DFT calculations) as shown in the inset of Fig. S7 (a). Based on the fact that the elastic constants C_{11} and C_{33} linearly depend on the intralayer and interlayer interactions respectively [25], by changing the intralayer and interlayer interactions of graphite according to the change of the elastic constants C_{11} and C_{33} with different defect concentrations as shown in the inset of Fig. S7 (a), the interfacial thermal conductance across the interface between Al and graphite as a function of the defect concentration of graphite is calculated using NEGF method as shown in Fig. S7 (a).

As can be seen in Fig.S7 (a), the calculated interfacial thermal conductance between

Al and graphite increases with the increasing defect concentration of graphite, confirming the hypothesis that the reduction of the elastic constants caused by the defect concentration of graphite contributes to the interfacial thermal conductance between Al and defected graphite. According to the defect concentration of 8.4% in case 1 estimated in the main text based on the decrease of Fermi levels and the DFT results, the interfacial thermal conductance between Al and milled graphite can be enhanced by 11.3 W/m²K as shown in Fig. S7 (a) due to the reduction of the elastic constants, and the enhanced value is still limited compared with 5 fold increasements of our measured results in main text. Also, the enhanced value of the calculated interfacial thermal conductance based on the reduction of the elastic constants is far less than the predicted value reported in previous literature [25]. This can be attributed to the different influences on the interfacial thermal conductance between the elastic constants C11 and C_{33} . As can be seen in the inset of Fig. S7 (a), both the elastic constants C_{11} and C_{33} decreases with the increasing defect concentration, and the elastic constant C₁₁ declines more severely than C₃₃. On one hand, the decrease of the elastic constants C₁₁ causes phonon in graphite to focus in the cross-plane direction, leading to the significant enhancement of the interfacial thermal conductance [25]. On the other hand, the decrease of the elastic constants C₃₃ causes phonon to defocus in the cross-plane direction, resulting in the decrease of the interfacial thermal conductance [25]. Although the decrease of the elastic constants C_{11} and C_{33} have different influences on the interfacial thermal conductance, the decrease of the elastic constant C₁₁ is more severe than the decrease of the elastic constant C₃₃, making the phonon focusing effect to be the major influence on the interfacial thermal conductance with the increasing defect concentration of graphite. The major influence of the phonon focusing effect has also been verified by the calculated iso-energy surfaces of graphite with different defect concentrations as shown in Fig. S7 (b-d). As the defect concentration of graphite increases, the sharp of the calculated iso-energy surfaces expands along the in-plane direction, contributing to the increase of the phonon group velocity component along the cross-plane direction, which enhances the interfacial thermal conductance across Al and the defected graphite.



Figure S7. (a) Interfacial thermal conductance across the interface between Al and graphite as a function of defect concentration of graphite. The inset is the calculated elastic constants C_{11} and C_{33} of graphite as a function of defect concentration using DFT methods. The red lines in the inset are the predictive trend by parabolic fitting with the DFT results at the defect concentrations of 0%, 6.25% and 12.5% respectively. (b-d) the acoustic iso-energy surfaces of graphite with different defect concentrations. The blue, green and red curves represent the longitudinal acoustic (LA), transverse acoustic (TA) and flexible acoustic (ZA) branches, respectively. The arrows represent the phonon group velocity vectors, which are perpendicular to the iso-energy surfaces. The coordinate scale represents the value of wave vector divided by the frequency, which is defined as same as previous literature [27].

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