Weaker bonding can give larger thermal conductance at highly mismatched interfaces

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Thermal boundary conductance is typically positively correlated with interfacial adhesion at the interface. Here, we demonstrate a counterintuitive experimental result in which a weak van der Waals interface can give a higher thermal boundary conductance than a strong covalently bonded interface. This occurs in a system with highly mismatched vibrational frequencies (copper/diamond) modified by a self-assembled monolayer. Using finely controlled fabrication and detailed characterization, complemented by molecular simulation, the effects of bridging the vibrational spectrum mismatch and bonding at the interface are systematically varied and understood from a molecular dynamics viewpoint. The results reveal that the bridging and binding effects have a trade-off relationship and, consequently, that the bridging can overwhelm the binding effect at a highly mismatched interface. This study provides a comprehensive understanding of phonon transport at interfaces, unifying physical and chemical understandings, and allowing interfacial tailoring of the thermal transport in various material systems.

INTRODUCTION

The rapid advances in electronics have triggered increasing demand for effective heat dissipation at the material level (1), for which interfaces between constituent materials and inside composites are critical because they are scatterers for phonons, resulting in thermal resistance (Fig. 1A) (2). To enhance the thermal boundary conductance (TBC), the insertion of an intermediate layer at an interface has attracted considerable interest. Controlling the mass (3), thickness (4–6), and chemical components (7) of the intermediate layer has been suggested to be effective in enhancing the TBC. Recently, the self-assembled monolayer (SAM) (8) comprising alkyl chain molecules with a thickness below 2 nm has emerged as a promising candidate for the intermediate layer (9–11) because of the precise and flexible controllability of the physical and chemical structures by varying the chain length and end groups (Fig. 1B).

The use of an SAM as an intermediate layer facilitates interfacial heat conduction through two distinct mechanisms: binding and bridging effects (12). Many studies have shown TBC enhancement by increasing the interfacial adhesion via the binding effect, which enhances the transmission coefficient of individual phonons while remaining the range of phonon transmission constant (the number of phonon channels keeps unchanged). At interfaces such as gold/quartz (13) and Cu/silica (14), by varying the end groups from CH3 [van der Waals (vdWs) interface] to SH (covalently bonded interface), which increases the interfacial adhesion strength by approximately two orders of magnitude, the TBC increases from 36 to 65 MW/m2·K, and from 260 to 430 MW/m2·K, respectively. In addition, fewer, but still several, works have demonstrated enhancement of the TBC through the bridging effect at interfaces such as gold/polymer (25 to 165 MW/m2·K) (15) and Cu/diamond (40 to 80 MW/m2·K) (16). Bridging the vibrational frequency mismatch between the materials on the sides of the interface with the SAM can extend the phonon transmission spectrum to a broader range, the same as that of the expanded vibrational density of states (vDOSs) overlap, which creates extra phonon channels for an enhanced interfacial thermal transport. Although previous studies have elucidated the effectiveness of SAM modification for TBC enhancement and corresponding mechanisms, the binding and bridging effects have always been discussed separately. A unified understanding of the relative contributions of the binding and bridging effects would expand the methods to further promote the TBC by SAM modification, but the challenge is to systematically vary both the bonding strength and frequency matching.

In this work, with fine control over the structure of the SAM, we realize a systematic study of the binding and bridging effects on the TBC by varying both the end groups of the SAM (CH3 and SH) and phonon frequencies of the dielectric (silicon, sapphire, and diamond). In the Cu/diamond system, we experimentally demonstrate that the CH3-SAM–functionalized vdWs interface gives a counterintuitively higher TBC than the SH-SAM–functionalized covalently bonded interface, whose interfacial adhesion strength is typically two orders of magnitude higher (17). By comparing the TBCs of all the systems, we find that this abnormal phenomenon only occurs at the interface with highly mismatched frequencies, where the bridging effect dominates over the binding effect in determining the TBC. We find a trade-off between the binding and bridging effects, and the strong bridging effect overwhelms the negative effect of the weak interfacial adhesion at the CH3-SAM–modified vdWs interface.

RESULTS

Anomalous heat conduction at the mismatched interface

To obtain an interface with variable adhesion, we used alkylsilanes [n-butytrimethoxysilane and 3-(trimethoxysilyl)propanethiol] with two different kinds of end groups (SH and CH3, respectively) for SAM functionalization (Fig. 1C). The SH-SAM can form a robust covalent bond (S–Cu) with Cu via the dehydrogenation reaction of SH, making the interfacial adhesion strength typically two orders of magnitude higher than that with the weak vdWs interaction between the CH3-SAM and Cu. Using these two kinds of SAM in systems such as Cu/diamond, Cu/sapphire, and Cu/silicon with different

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of the SAM influences the heat conduction through the interface (10), SAM formation on the substrates (diamond, sapphire, and silicon) was performed concurrently in the same reaction container to ensure that the morphologies of the SAMs in all the systems are comparable. The morphologies of the SH-SAM and CH\textsubscript{3}-SAM should be similar to ensure that the resultant differences in the TBC originate mainly from the differences in the properties of the SAM end groups. To this end, before depositing the metals, we applied the commonly used water contact angle and ellipsometry measurements to characterize the SAM morphologies (Fig. 2A). The thicknesses of both the SH-SAM and CH\textsubscript{3}-SAM are approximately 5 to 6 Å, with contact angles of 53° and 93°, respectively, owing to the difference in the hydrophilicity of the end groups. This result agrees well with a previous study (18), indicating that the SH-SAM and CH\textsubscript{3}-SAM are similar in morphology, uniform monolayers with high order.

Using time-domain thermoreflectance (TDTR; Fig. 1D), we first measured the TBC at the Cu/diamond interface. The temperature decay profile illustrates a clear difference between the interfaces functionalized by the SH-SAM and CH\textsubscript{3}-SAM (Fig. 3A), where the decay is considerably faster in the CH\textsubscript{3}-SAM case. This result indicates an unexpected phenomenon in which the CH\textsubscript{3}-SAM–modified interface with the CH\textsubscript{3}-Cu vdWs interaction, whose adhesion is two orders of magnitude lower than the S-Cu covalent bonding, achieves a higher TBC than the SH-SAM–modified interface. This contradicts the fundamental understanding of the binding effect reported in previous studies (13, 14).

To verify the reproducibility of the experimental results, we carried out additional measurements using independently prepared samples of the same kind. The resulting TBCs are summarized in Fig. 3B. For each case, the measured TBC was observed to be within a reasonable range (±7 MW/m\textsuperscript{2}K; where the error bars represent the uncertainty in TDTR data fitting and sample preparation, including SAM formation and metal deposition), with an average TBC for the CH\textsubscript{3}-SAM interface of approximately 61.5 MW/m\textsuperscript{2}K, twofold higher than that of the SH-SAM interface (33.6 MW/m\textsuperscript{2}K). This high reproducibility of the experimental results proves the
Figure 3C shows the TBCs in Cu/sapphire and Cu/silicon systems. We found that the TBC shows the usual dependence on the interfacial adhesion strength (9, 13, 14) in that the interfaces modified by the SH-SAM (covalently bonded interfaces) have higher TBC than those modified by the CH3-SAM (vdW interfaces). This result once again supports the reliability of the anomalous trend of the TBC observed for the Cu/diamond system because the sample preparations for all the systems were performed together.

The systems with different materials on the dielectric side of the interface result in different extents of vibrational frequency mismatch between Cu and the dielectric. This influences the bridging effect of the SAM (20–23) due to the difference in the overlapping of vibrational frequencies between the SAM and the materials on both sides, which can change the TBC. In this sense, the results may imply that the bridging effect of the CH3-SAM has such a strong impact that it overwhelms the disadvantage of the weak vDWs interaction in terms of the binding effect.

### Phonon transport at interfaces with varying phonon frequencies

For the discussion in view of the vibrational mismatch between different materials, we use the Debye temperature, which is the temperature at which all vibrational modes are excited in a given material, as an indicator for the frequency range of the lattice vibrational spectrum (or vDOSs). Here, as a simplification, the degrees of vibrational mismatch of the systems are determined by the Debye temperature (19) of the materials on the dielectric side, which is 550, 1000, and 2200 K for silicon, sapphire, and diamond, respectively, as the other side was fixed to Cu (Debye temperature is 343 K). Because the measured TBC for the Cu/silicon systems is underestimated, as it includes the thermal resistance of the unavoidable natural oxide layer (~3-nm-thick silica, measured by the ellipsometer), the value was corrected by removing the thermal resistance of the oxide layer. We then plotted all the TBCs as a function of the Debye temperature of the dielectric side (Fig. 3D). In the SH-SAM–functionalized cases, an increase in the vibrational mismatch of the system results in a reduction in the TBC. This result agrees well with the previous research that studied the TBC between metal leads with different vibrational frequencies (24). In contrast, for the CH3-SAM–modified cases, the trend becomes nonmonotonic, where the highly mismatched Cu/diamond interface shows a higher TBC than the interfaces with lower degrees of vibrational mismatch. According to previous studies (25, 26) on highly mismatched metal/diamond systems, the heat conduction through the interface is dominated by the inelastic phonon interaction, resulting in low TBC, which means that phonon transmission through the elastic channel is strongly impeded by the vibrational mismatch. Therefore, if the CH3-SAM modification can substantially enhance the bridging effect, then phonon transmission can be promoted through elastic phonon channels to largely affect the TBC, even to the extent that the loss in the binding effect is overwhelmed. This makes a highly mismatched system a necessary condition for the bridging effect to overwhelm the binding effect, which is consistent with the superiority of CH3-SAM modification over SH-SAM modification observed only for the Cu/diamond interface.

To further examine the mechanism, we performed molecular dynamics (MD) simulations of the Cu/diamond system (see Materials and Methods). The MD simulations capture the experimentally observed trend of the TBC in the two different SAM cases, where the...
TBC is higher for the CH$_3$-SAM (151.2 MW/m$^2$K)–modified case than for the SH-SAM case (110.4 MW/m$^2$K). Using this system, we calculated the vDOSs of Cu, diamond, and the SAM (Fig. 4A). The vDOS of diamond exhibits high peaks at frequencies around 40 THz, totally deviating from that of Cu, whose cutoff frequency is approximately 8 THz. The vDOSs of the CH$_3$-SAM and SH-SAM show a broad distribution (0 to 90 THz), where the vDOS overlap with that of diamond is notable for both kinds of SAM. This makes the temperature jumps at the SAM/diamond interface negligible. In contrast, a relatively large temperature jump occurs at the Cu/SAM interface (fig. S1), dominating the TBC of the entire interface. Therefore, the vDOS overlap of Cu and the SAM, which determines the number of elastic phonon channels at the interface, becomes the key factor of the TBC. Consequently, we mainly focus on the low-frequency range (~20 THz) covering the vibrational modes of both the SAM and Cu, where an evident difference in the vDOSs exists between the SH-SAM and CH$_3$-SAM. For the CH$_3$-SAM, the vDOS is higher in the range of frequency overlap with that of Cu (~8 THz), with a minor drop below 2 THz, which benefits the bridging effect. The vDOS of the SH-SAM decreases more rapidly with decreasing frequency, resulting in a smaller vDOS than that of the CH$_3$-SAM below 8 THz, thus unfavorable vibrational matching with Cu and a weaker bridging effect. Here, the calculated magnitude of the difference in vDOS between CH$_3$-SAM and SH-SAM is somewhat smaller than the actual experiment judging from the difference in TBC (~20%), as shown in Fig. 4B, being smaller than that of the experiments (twofold). This is understandable considering that the vDOSs of SH-SAM and TBC of CH$_3$-SAM are highly sensitive to the force fields of the MD simulations as shown in Fig. 4B and fig. S2, respectively, which will be discussed further later. Therefore, here, we intend to use the MD simulations only to qualitatively reproduce the experiment and explain the roles of the bridging and binding effects.

This difference in vDOS between the SH-SAM and CH$_3$-SAM can be explained by the low-frequency vibrational modes of the SAM, whose frequencies are roughly proportional to $\sqrt{k/m}$ (15). Here, $m$ is the effective atomic mass of SAM molecules, and $k$ is the effective force constant of the entire SAM layer considering it as a spring system connecting Cu and diamond (the model is concretely discussed in the Supplementary Materials). Because both ends of the SH-SAM chain molecules are anchored through strong covalent bonds, the effective force constant $k$ is large. In contrast, the CH$_3$-SAM molecules are covalently bonded only on a single side (the other side experiences the weak vdWs force interaction), making the effective force constant $k$ smaller. Therefore, as the masses of these two kinds of SAM are similar (13% difference), the smaller effective force constant in the case of the CH$_3$-SAM can induce lower vibrational frequencies, hence resulting in a higher bridging effect. This idea was further verified by the change of vDOS through artificially changing the bonding strength of Cu–S indicated by the coefficient of the harmonic bond between Cu and S in the MD simulation. By substantially increasing or decreasing this bonding strength (by 0.1 and 10 times), we observed a clear downshift of the low-frequency vibrational modes with increasing bonding strength between the SAM and Cu (fig. S2A). This result indicates the thought-provoking fact that strong interfacial adhesion inhibits heat conduction by weakening the bridging effect at the interface, giving rise to an unexpected trade-off between the binding and bridging effects. Note here that the vDOS variation when artificially changing the interaction of CH$_3$-SAM and Cu is negligibly small (fig. S2B). The spring model introduced above can also explain the difference of vDOS variation between the CH$_3$-SAM and SH-SAM (discussed in the Supplementary Materials). This result can further verify the effectiveness of the spring model in describing the vibrational frequency of SAM.

**Bridging and binding effect**

To further elucidate the contributions of the bridging and binding effects in the highly mismatched system, we artificially change the mass of Cu in the MD simulation to alter the extent of vibrational mismatch of Cu/diamond system. The vDOS of copper upshifts with the reduction of the copper mass (fig. S6A), which reduces the extent of vibrational mismatch at the Cu/SAM interface for both the CH$_3$-SAM and SH-SAM cases. This enables isolated control of the bridging effect and helps us to separately discuss the effect of bridging and binding effect. With the decreasing mass of copper, the TBC of SH-SAM–modified systems increases faster and eventually exceeds the TBC of CH$_3$-SAM cases (fig. S6B). These results indicate that the bridging effect plays more critical role for the system with a larger extent of vibrational mismatch.

Alternatively, we studied the variation of TBC for both the CH$_3$-SAM and SH-SAM–modified cases with increasing interfacial adhesion
strength (Fig. 4B). For the CH$_3$-SAM case, because adjusting the interfacial adhesion strength exhibits negligible influences on the vDOS (fig. S2B), only the binding effect is modified. Hence, the TBC increases rapidly when increasing the interfacial adhesion strength (as described in Materials and Methods), which indicates that the mode bridging between Cu and the SAM in this case is already fairly satisfied, and thus, enhancement of the binding is effective in further enhancing the TBC. On the other hand, in the case of SH-SAM, the increase in interfacial adhesion strength does not enhance the TBC. Note that the increase in interfacial adhesion strength does alter and shift the vDOS but in the direction to further enlarge the vDOS mismatch (fig. S2A). This verifies that TBC becomes insensitive to the interfacial adhesion strength when vDOS mismatch is large. The above analyses of CH$_3$-SAM and SH-SAM together confirm that the bridging effect is more critical in highly mismatched systems for enhancing the TBC.

We also calculated the spectral interfacial thermal conductance to confirm the dominant phonon frequencies that contribute to the TBC (Fig. 4C). For all cases, the spectral interfacial thermal conductance is mainly distributed within 0 to 8 THz, below the cutoff frequency of bulk Cu. In addition, the CH$_3$-SAM-modified interfaces demonstrate higher spectral interfacial thermal conductance within 0 to 8 THz, which agrees with the above discussion that the elastic phonon transport enhanced by the CH$_3$-SAM at the Cu/SAM interface dominates the TBC. Notably, a minor but non-negligible spectral interfacial thermal conductance is observed above 8 THz (up to approximately 14 THz), which is also enhanced by increasing the interfacial adhesion for both cases. The transmission above the cutoff frequency of bulk Cu should be due to the surface states of Cu being influenced by the mode hybridization with the SAM, and an inelastic process also possibly exists (27); however, we would like to stress that the contribution of the transmission in the frequency of 8 to 14 THz to the overall TBC is minor and the trade-off between the bridging and binding effects in this system can be well explained in terms of an elastic process based on bulk Cu vibrational states.

DISCUSSION

We have experimentally observed an unusual heat conduction behavior in that a vdW interface with weaker interfacial adhesion provides a higher TBC than the strong covalently bonded interface obtained by SAM functionalization. To elucidate the mechanism responsible for this abnormal behavior, we found that the contributions of the bridging and binding effects to TBC enhancement depend strongly on the degree of vibrational mismatch of the interface. The substantial bridging effect in the highly mismatched Cu/diamond interface can offset the negative effect of the weak binding and further enhance the TBC because the bridging effect is more critical in determining the TBC in the highly mismatched system. In addition, we found the usually ignored fact that a trade-off exists between interfacial adhesion and the bridging effect by controlling the SAM structure for highly mismatched systems. The results lead us to make an important practical suggestion when designing an intermediate layer for considerable TBC enhancement. Whenever combining the materials commonly used in electronic devices, such as silicon carbide, boron nitride, and aluminum nitride, whose Debye temperatures exceed 1000 K, with other materials with low cutoff frequency, the bridging effect may become dominant in enhancing the TBC. This study established a comprehensive model for interfacial heat conduction enhancement by an intermediate layer, applicable to thermal management materials in various systems.

MATERIALS AND METHODS

SAM formation

Two kinds of silanes [$n$-butyltrimethoxysilane and 3-(trimethoxysilyl)propanethiol] were used as the precursors for the formation of the CH$_3$-SAM and SH-SAM, respectively. The process was as follows. First, dielectric substrates (diamond, sapphire, and silicon) were immersed in piranha solution (30% H$_2$O$_2$ + 70% H$_2$SO$_4$ for 2 hours), followed by ultrasonication washing using deionized water and acetone solution (99.5%) in sequence. The substrates were then baked (100°C) for 30 min to obtain a clean hydroxy-enriched surface with a monolayer of water. Second, SAM functionalization was performed on the substrates. The processes for the two kinds of SAM formation were different because of the different chemical reactivities of the end groups. For the CH$_3$-SAM, substrates were first immersed in a 30-ml toluene solution (99.5%; Wako) with 30 µl of $n$-butyltrimethoxysilane (Gelest) and 45 µl of triethylenesilane (99.5%; Sigma-Aldrich) for 48 hours in a sealed container. For the SH-SAM, substrates were immersed in a 30-ml toluene solution (99.5%; Wako) with 5 µl of 3-(trimethoxysilyl)propanethiol (TCI), 45 µl of triethylamine, and 0.01 mg of dithiothreitol (Sigma-Aldrich) for 2 hours [the short process time and the addition of dithiothreitol were to prevent oxidation and aggregation of 3-(trimethoxysilyl)propanethiol]. Last, the SAM-functionalized substrates were washed with toluene and acetone solution using ultrasonication in sequence to remove the physically adsorbed silane. SAM formation on different substrates was carried out in the same vessel in the same manner. Independent preparation was performed several times to verify the reproducibility of the SAM formation. The diamond (EDP), silicon (Nilaco), and sapphire (Amanda Namiki) dielectric were used as the substrates. The diamond substrate was synthesized by a plasma chemical vapor deposition process, guaranteeing a high-quality single crystal with less nitrogen impurity (<8 parts per million) and hence a high thermal conductivity of 2000 W/m·K. After the SAM formation, we deposited the Cu and aluminum in sequence using electron-beam (EB) evaporation (VTR-350MERH, ULVAC) under pressure below 10$^{-3}$ Pa.

Characterization of the SAM morphology

Before the deposition of the metal layers, the thickness of the SAMs was evaluated by ellipsometry measurements (MARY-102, Five Lab), and 25 points on the substrates were measured for each sample to obtain the average thickness. In addition, the deionized water contact angle measurement was used for characterization of the SAM morphology (e.g., order of SAM alignment) because the hydrophilicities of the CH$_3$ and SH end groups are different. After metal deposition, we observed a cross-sectional view of the interfaces. The Cu/SAM/diamond samples were processed by the focused ion beam method to obtain an ultrathin section of the interface. The sample was then attached to a grid and measured by TEM (JEM-ARM200F, JOEL) with elemental mapping performed by EDX. The SAM/Cu chemical bonding was evaluated using XPS (PHI-5000 VersaProbe III, ULVAC) equipped with an argon-ion sputtering system. Because the penetration depth of XPS measurement is small (several nanometers), to directly probe the chemical bonding at the Cu/SAM interface, we used a precisely controlled sputtering process to etch the metal layer and obtain a new surface near the SAM/Cu interface, assisted by in...
situ XPS monitoring. The XPS spectrum was calibrated on the basis of the carbon 1s peak to obtain the accurate chemical shift of the sulfur 2p peak. We could then evaluate the chemical bonding by the chemical shift of the peaks in the XPS spectrum.

**Time-domain thermoreflectance**

TDTR, a pump-probe method, was applied to measure the TBC at the Cu/dielectric (diamond, silicon, and sapphire) interfaces. In the TDTR setup used in this study, the laser frequency was 80 MHz, with a pulse width of 140 fs. The diameters (1/e² radius) of the pump (400 nm) and probe (800 nm) lasers focused on the surface of the sample were 39 and 10 μm, respectively. The pump laser modulation was conducted with a high frequency of 11.05 MHz, which resulted in a small penetration depth and hence provided a high sensitivity for the TBC at the Cu/dielectric interfaces (because the targeted interface is close to the top surface of the sample). This was proven by the sensitivity calculation result (fig. S3), which suggests a high sensitivity for the TBC of the Cu/dielectric interface (the detailed structure used for TDTR analyses will be described later) and hence high reliability of the resulting TBC value. Aluminum (Al) (80 nm)/Cu (20 nm)/dielectric (diamond, silicon, and sapphire) (1 mm) samples were used for the TDTR measurement. Because the thermal resistance of the Al/Cu interface is negligibly small [2.7 × 10⁻⁸ m²K/W (28)] such that it can be ignored in the heat conduction model, regarding the Al and Cu layers as one to simplify the heat conduction model to a two-layer structure is reasonable. To extract the targeted TBC value by fitting TDTR data, we used the temperature decay profile with a delay time longer than 200 ps to avoid the influence of the electron-phonon interaction process (29).

The parameters for fitting are as follows. The bulk values of the specific heat capacity and thermal conductivity were used for the metal and the dielectric layer (diamond, silicon, and sapphire). The thickness of the transducer (~100 nm) was obtained by measuring the reference sample (Al/Cu/quartz), whose metal layers were deposited concurrently with the Al/Cu/SAM/dielectric samples.

**MD simulation**

Nonequilibrium MD (NEMD) (30) simulations were performed to study the TBC in the Cu/SAM/diamond system using the LAMMPS package (31). The size of the Cu and diamond lead was 5.0 nm by 5.0 nm by 50.0 nm. The diamond surface was fully hydroxylated and initially used as the starting point to graft alkylsilane(-OSi(OH)₂(CH₃)₃CH₃). The embedded atom method potential (32) and Tersoff potential (33) were used to describe the covalent bond interactions between Cu atoms and carbon atoms inside the diamond, respectively. The OPLS (Optimized Potentials for Liquid Simulations) all-atom model (34, 35) was applied to build the force field parameters of hydroxyl groups and alkyl chains. The Lennard-Jones (L-J) potential parameters between different atoms were described by the geometric combination rule. The particle-particle mesh Ewald summation method (36) assisted the calculations for slab geometries (37).

The system was first relaxed in the isothermal-isobaric (NPT) ensemble. After the systems reached equilibrium with no stresses remaining, the NEMD simulation was performed. Periodic and fixed boundary conditions were applied along the x direction and along the y and z directions, respectively. To generate a temperature difference, the atoms at the two ends of the system were coupled with Langevin thermostats at temperatures T_H and T_L. In our simulations, we set T_H = 330 K and T_L = 270 K to calculate the TBC at 300 K. After the system reached the steady state, the cumulative energy ΔE added to/subtracted from the heat source/sink region was recorded for 2.5 ns. The time step was set as 0.5 fs. By applying a linear fitting to the raw data of the cumulative energy ΔE, the energy change per unit time (ΔE/Δt) was obtained, which was used to calculate the heat flux J = ΔE/(Δt·S). Here, S is the cross-sectional area of the simulation domain. The TBC was calculated by J/ΔT, where ΔT and J are the temperature difference at the interface and the magnitude of the heat flux, respectively.

**Spectral interfacial thermal conductance calculation**

The spectral interfacial thermal conductance T(ω) was calculated as (38)

\[
T(\omega) = \frac{q(\omega)}{k_B \Delta T}
\]

where \(k_B\) is the Boltzmann constant and \(\Delta T\) is the temperature difference at the interface of Cu and the SAM because the TBC of the Cu/SAM/diamond system is dominantly governed by the Cu/SAM interface (fig. S1). Here, \(q(\omega)\) is the frequency-dependent heat current across the interface, which can be calculated as (39, 40)

\[
q(\omega) = \frac{2}{\hbar} Re \sum_{j} \langle \mathbf{F}_{ji}(\omega) \cdot \mathbf{v}_{i}(\omega)^* \rangle
\]

where \(t_s\) is the simulation time and \(\mathbf{F}_{ji}\) is the interatomic force on atom \(i\) due to atom \(j\). Note that the \(\mathbf{F}_{ji}\) and \(\mathbf{v}_{i}\) are obtained directly during the execution of the MD simulations. Therefore, in our simulations, the anharmonic effect has been considered in the calculation of phonon transmission.

**vDOS calculation**

The vDOS was calculated according to vDOS (ω) = FFT [Cor(t)], where FFT denotes the fast Fourier transform and Cor(t) is the normalized velocity autocorrelation function. Cor(t) can be described as

\[
Cor(t) = \frac{\sum_{i=1}^{n} m_i \mathbf{v}_{i}(t) \cdot \mathbf{v}_{i}(0)}{\sum_{i=1}^{n} m_i \mathbf{v}_{i}(0) \cdot \mathbf{v}_{i}(0)}
\]

where \(t\) is the correlation time, \(n\) is the number of atoms, \(m_i\) is the mass of the \(i\)th atom, \(\mathbf{v}_{i}\) is the velocity vector of the \(i\)th atom, and the bracket denotes the ensemble average.

**Artificial control of the interfacial adhesion strength**

We artificially modified the interfacial adhesion strength in the MD simulation to observe the variation in the TBC and vDOS. For the interfaces functionalized by the SH-SAM, because the vdWs interactions between Cu and carbon and hydrogen atoms are much weaker than the covalent bond between Cu and sulfur atoms, we can neglect the influence of the vdWs interaction and only adjust the coefficient \(k\) of the harmonic bond between Cu and S atoms to change the interfacial adhesion strength. For the case of the CH₃-SAM, we modified the coefficient \(\epsilon\) of the L-J potential between Cu and all the carbon and hydrogen atoms of the SAM to change the interfacial adhesion strength.

To verify the effect of the bonding strength in determining the bridging effect, we significantly changed the interfacial adhesion...
strength by 0.1 and 10 times in the case of the SH-SAM to observe a clear shift of the vDOS spectra. In contrast, in the discussion about the superiority of the binding and bridging effects in the highly mismatched system, we calculated the TBC under different interfacing adhesion strengths for both CH3-SAM and SH-SAM-modified interfaces in a relatively small range (within three times) because overly increasing the interfacing adhesion strength (such as by 10 times) may result in an upshift of the vDOS spectra of the SAM and thus weaken the bridging effect. This can avoid making the discussion more complicated (i.e., by fixing the bridging effect and only modifying the bonding strength) and enable us to discuss the bridging and binding effects individually.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/17/eaabf197/DC1

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