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Preview

Bridging overwhelms binding for enhancing thermal boundary conductance

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How to enhance the thermal transport across interfaces? There is a common sense that increasing the interfacial bonding strength can facilitate the phonon transport. Recently in Science Advances, Shiomi and colleagues experimentally reported a counterintuitive discovery that a weak bonded interface can transport more heat than a strong bonded interface via the bridging effect rather than the binding effect in a highly mismatched heterointerface. The comprehensive and inspiring advance on interfacial heat transport is highlighted, and some brief introduction of the state-of-the-art progress, challenges, and future directions are outlined for the thermal management of nanoelectronics and nanoelectromechanical systems.

Heterointerfaces have been explored intensively for developing functional devices and revealing novel physical/chemical effects therein, like superlattices, multiple quantum wells, photonic crystals, electromagnetic metamaterials, field-effect transistors, high electron mobility transistors, light-emitting diodes, laser diodes, solar cells, triboelectric nanogenerators, etc.[1–4] Nevertheless, heterointerfaces have become the key bottleneck for the heat transport especially when the characteristic dimensions are approaching nanoscale downwardly, even at the magnitude of electron or phonon mean free paths, where the interfacial thermal resistance plays an increasingly dominant role along the heat dissipation paths.[1] To enhance the thermal boundary conductance (TBC) between two solid interfaces, people have proposed to inset the soft organic self-assembled monolayer (SAM) in the nanoscale dimension to form covalent bonds rather than the weak van der Waals (vdWs) bonds at the interfaces with nearly several times of improvement of TBC in most heterointerfaces.[5–7] The SAMs, consisting of a headgroup, a hydrocarbon chain, and a tail group, can tailor the surface chemical and physical properties, thus enabling the functionalizing of solid materials with enhanced interfacial binding strength significantly. For decade, people have been accustomed to an inertial thinking that stronger interfacial binding strength via the covalently bonded SAM can facilitate the improvement of TBC for all heterointerfaces. Recently, writing in *Science Advances*, Junichiro Shiomi and colleagues — who are based at institutes in Japan and Hong Kong, said NO to this common sense by reporting a counterintuitive experimental discovery that TBC of a weak vdWs-bonded interface is larger than that of a strong covalently-bonded interface, which is attributed to the overwhelming bridging effect over the binding effect at a highly mismatched interface.[8]

For a metal-SAM-dielectric/semiconductor junction, electrons are usually insulated and phonons are the only heat carriers. The corresponding TBC across the junction can be described by the Landauer transport formulism, involving with the density of state of phonons, the ballistic/diffusive phonon transport nature in the SAM, the frequency-dependent phonon transmission windows, and the interfacial binding strength. Actually, adding SAM as an intermediate layer to enhance TBC involves with two mechanism: binding effect and bridging effect. The binding effect can enhance the transmission coefficient of individual phonons without influencing the phonon transmission window to increase TBC, while the bridging effect can extend the phonon transmission window to allow more phonon channels to enhance TBC. Historically, the binding effect has been demonstrated effective via the covalent bond for facilitating TBC enhancement in most heterointerfaces, like gold/quartz, gold/titanium dioxide, gold/graphene oxide, copper/silica, copper/silicon, copper/sapphire, etc.[5,6] In contrast, there are few works that report the importance of bridging effect via the vdWs bond in gold/polyethylene and copper/diamond interfaces.[7] Although both effects have been recognized in previous studies for TBC enhancement, they haven't been discussed systematically.

Experimentally, Shiomi and coworkers systematically investigate the binding effect and bridging effect on the TBC enhancement by subtly tuning the tail group of the SAM (vdWs bond with -CH_3, and covalent bond with -SH) between the copper-SAM-dielectric (silicon, sapphire, and diamond) junction, as shown in Figure 1A. The -SH tail can covalently bond with copper via the dehydrogenation reaction with two

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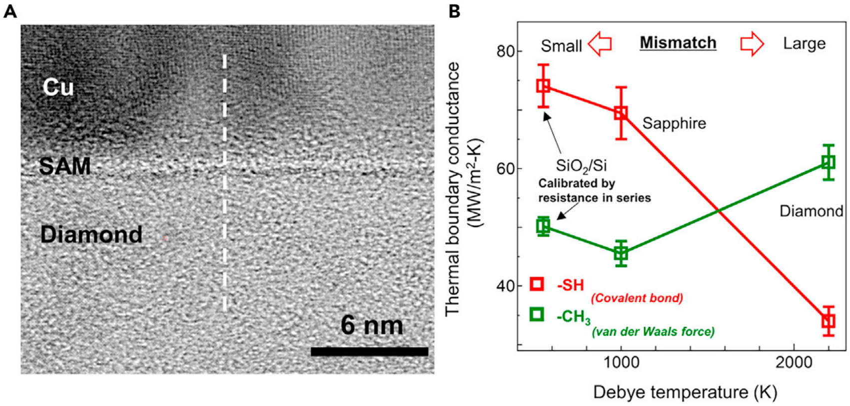

Figure 1. Heterointerface and thermal boundary conductances

(A) High-resolution transmission electron microscopy image of the copper-SAM-diamond junction and (B) Thermal boundary conductance measurements of different heterointerfaces with varying SAMs and Debye temperatures. Reproduced with permission from Ref.[8]

order of magnitude of larger interfacial binding strength than the vdWs bond between the -CH_3 tail group and copper. In all the experiment, the thickness of the SAM layer is kept approximately at 5~6 Å to remove the intermediate thickness influence on the TBC measurement. Through time-domain thermoreflectance (TDTR) measurement, the TBC of copper/silicon and copper/sapphire interfaces with covalent bond are higher than that with vdWs bond without accident, while the TBC of copper/diamond interface with covalent bond is lower than that with vdWs bond surprisingly. To analyze the underlying physics, they relate the TBC measurements with the Debye temperature, which is sign of phonon vibrational mismatch between the copper (343 K) and the dielectric materials (550, 1000, 2200 for silicon, sapphire, and diamond, respectively), as shown in Figure 1B. Their results reveal that the competition between the binding (covalent bond) and the bridging (vdWs bond) effects is influenced by the phonon vibrational mismatch of the heterointerface materials, and in highly mismatched interfaces the bridging effect overwhelms.

The key merit offered in their work is that they take consideration of the phonon transmission window of the heterointerface materials and establish the relationship between the TBC and the Debye temperature (a sign for vibrational mismatch). Most previous studies focus on single type of metal/dielectric interfaces with varying covalent-bonded or vdWs-bonded SAMs by changing the tail groups like -CH_3, -NH_2, -Br, -SH, and -OH, thus unable to reveal this important relationship[5]. Hints from this study are that although binding effect dominates in most heterointerfaces (with less mismatched phonon transmission windows), the bridging effect plays a more important role for the heterointerface with a large mismatch of phonon transmission window, revealing the unexpected yet significant trade-off therebetween. When the phonon vibrational mismatch is large, TBC is no longer sensitive to the enhancement of the interfacial binding strength but to the vibrational phonon mismatch instead.

The comprehensive investigation, which discusses the TBC dependence of interfacial covalent/vdWs bonds and vibrational phonon mismatch of heterointerfaces, suggests the important trade-off between the binding and the bridging effect depending on the heterointerface materials. Such finding is, in principle, straightforward yet profound for the thermal management of nanoelectronics. Intensifying the interfacial binding strength may be unavailing, and covalently bonded SAMs are not inevitable. Bearing such lessons in mind, we will feel more enlightened and flexible when designing SAMs for TBC enhancement. For practical application, more work needs further exploring in this domain, like quantifying the heterointerface smoothness, extending to other metal-dielectric/semiconductor junctions and dielectric-dielectric junctions, integrating SAM into electronic devices with balanced opto/electronic performance, developing reliable and scalable manufacturing process, etc. In particular, wide-bandgap semiconductors with high Debye temperatures, like gallium nitride (898 K), aluminum nitride (1150 K), silicon carbide (1146 K), boron nitride (1700 K), gallium oxide (738 K), and magnesium oxide (750 K), should be examined.[9] Furthermore, it is also worthy to exploring the transport characteristics of other carriers across the heterointerfaces in a similar way, which will enable broader impact to the whole nanoelectronics and nanoelectromechanical systems communities.

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