

The scientific impact of this project is to develop the fundamental underpinnings to achieve the rational design and high-efficiency of heat exchanger using multi-phase systems. The proposed work focuses on verifying the hypothesis of an interfacial heat exchange dominant regime at the nanoscale. In order to determine the dominant factors that affect the overall thermal performance, we have studied how vibrational spectra coupling, interfacial bonding, and structural orientation affect the heat transport across interfaces [1-2]. In addition, we have developed advanced spectroscopy method [3] to characterize the energy transport properties across different nanostructures and materials. More recently, we further investigate the microscopic structural relationship for interface heat transfer by combining our newly developed ultrafast optical spectroscopy and ab initio calculations based on molecular dynamics and density functional theory [4-6].

We have demonstrated for the first time a systematic characterization of heat exchange at the interface between anisotropic structures through the quantification using both experiment and theory [4]. To investigate the intrinsic heat transfer, we have fabricated atomically clean interfaces (Figure 1). In particular, highly anisotropic structures enable our study of the correlation between heat transfer and the intrinsic vibrational spectra. For example, black phosphorus has a puckered orthorhombic crystal structure where each P atom forms three covalent bonds with its neighbor P atoms from the 3p orbitals. Our recent work has also verified an anisotropic thermal conductivity [2] as a result of the non-uniform bonding: The longer bond connects P atoms in the top and bottom planes, and the shorter bond connects the nearest P atoms in the same plane; the different lattice layers are hold by van der Waals forces.

We have performed ultrafast pump-probe spectroscopy experiments to quantify the interface heat transfer by measuring the thermal boundary resistance (TBR). TBR is the key fundamental metric that measures an interface's resistance to thermal flow and results from the scattering of energy carriers, due to the difference in vibrational or other energy band structures from both sides of the interface. Using our newly developed AB-TDTR

technique [3], we were able to measure TBR along different directions. In our setup, a femtosecond laser pulse is split into a pump beam and a probe beam. The pump beam instantaneously heats up the sample surface, and the probe beam detects the sample temperature by utilizing the linear relationship between temperature and reflectivity. The delay time between pump and probe beams can be precisely controlled by a mechanical delay stage with a sub-picosecond resolution. Thus, the temperature

decay curve after the pulse heat source can be continuously recorded. By fitting the transient AB-TDTR signal to a multilayer heat conduction model, TBR is determined. Three typical sets of experimental data and their corresponding fittings for different directions are shown in Figure 2b. Surprisingly, a record-high ratio of anisotropic TBR was observed for different orientations as shown in Figure 3c. TBR in the cross-plane direction is  $1.62 \times 10^{-8} \text{ m}^2\text{KW}^{-1}$ , 2.41 times of that in the AC direction ( $6.71 \times 10^{-9} \text{ m}^2\text{KW}^{-1}$ ) and 3.27 times of that in the ZZ direction ( $4.95 \times 10^{-9} \text{ m}^2\text{KW}^{-1}$ ). This is the highest anisotropy ratio of

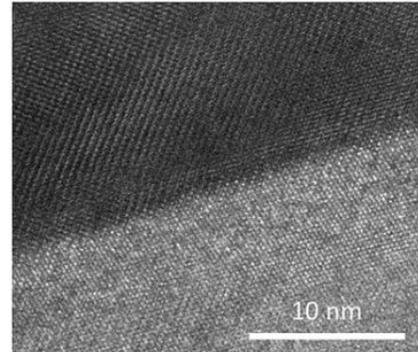


Figure 1. Our developed atomic-level clean interface for heat transfer measurement [4].

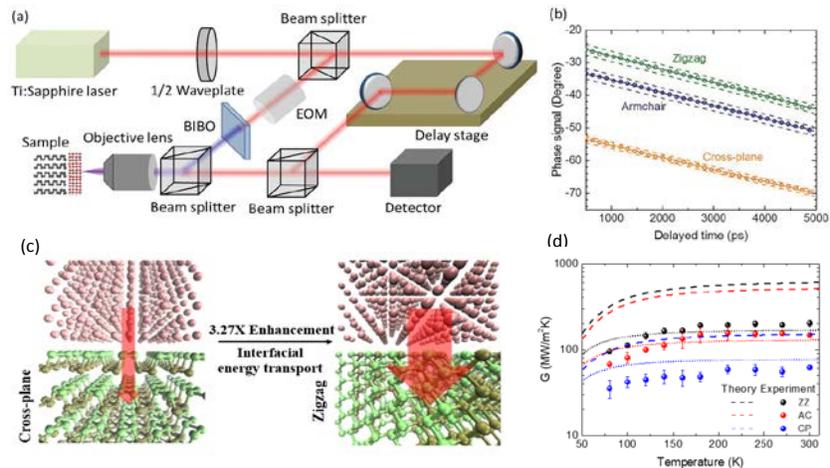


Figure 2. Experimental characterizations of interfacial heat transfer across interfaces along different directions [4].

TBR that has been reported in literature across the same material. Moreover, we have performed the temperature dependent measurement of TBRs in each direction from 80 to 300 K as shown in Fig. 3d. The anisotropy of TBR along different orientations remains remarkable for the full temperature range.

As a further step, we constructed atomistic modelling to analyze the data from experiments and understand the fundamental mechanisms of the interface heat exchange. We performed theoretical calculations based on density functional theory (DFT) and lattice dynamics to obtain the phonon band structures (Figure 3a-d). From the band structure, we found that the vibrational energy is highly different along different directions. The maximum frequency of acoustic phonons is around 2 THz along CP direction and 6 THz along ZZ direction, leading to much higher phonon travelling velocity along ZZ direction than CP direction as shown in Figure 3e. The anisotropy of both phonon group velocity and phonon density of states (DOS) (Figure 3f) both play an important role in the anisotropic interface transfer. Using diffuse mismatch model, the TBRs along different crystal directions can be predicted and shows a good agreement with experimental results (Figure 3g). Note that the vibrational spectra are not the only factor determining TBR. Hence, we performed non-equilibrium molecular dynamics (MD) simulation to study how the interface bonding affects the thermal transport across different phases. In the MD simulation domain illustrated in Figure 3h, interface is sandwiched by two blocks, at the centers of which there is a heat source and a heat sink respectively. A periodic boundary condition is applied to all the directions. Application of heat current through the heat source to the heat sink forms a temperature gradient along the direction normal to the interface. By monitoring the temperature drop across the interfaces and thus the TBR are predicted by the MD simulation (Figure 3i). The MD simulation results verified that the interface bonding energy has a strong effect on anisotropic interface transport. We found that increasing the interface bonding can lead to a larger interface heat transfer rate. Once the interface is weakly bonded, the TBR along ZZ direction is smaller than that along AC direction and the TBR along CP direction is largest, which further confirmed our experimental observation. With these experiment and modeling, our study provided important understanding of the relationship between heat transfer and material structures, opening up new opportunities in improving interface heat exchange and revising modeling predictions [5].

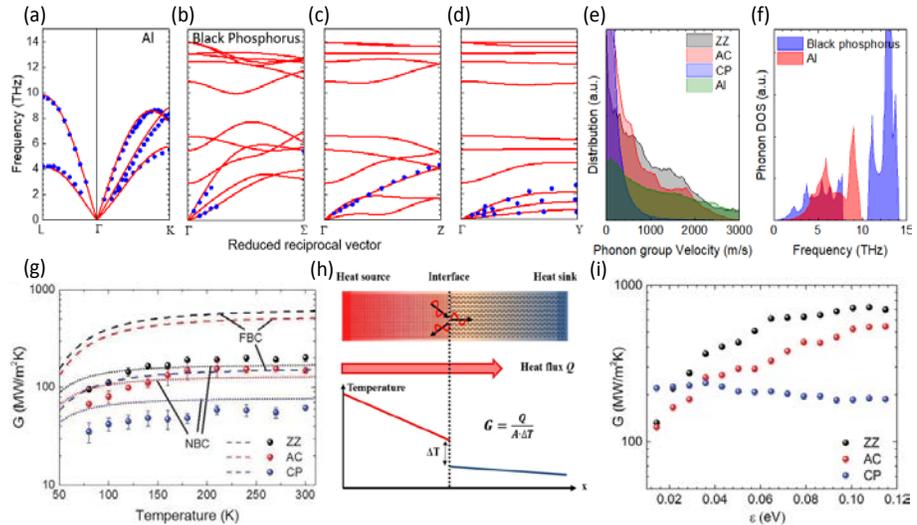


Figure 3. Atomistic modelling of interfacial thermal transport, in comparison with the theory results from DFT calculations and MD simulations.

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Professional career impact: For the PI, the support from ACS-PRF grant has allowed him to start this highly interdisciplinary project that integrates theory, transport characterizations, and molecular chemistry to investigate the coupling interactions of interfaces. This study has led to new fundamental understandings and several extended research directions in the PI's group, which has also resulted in a series of journal publications [1-6]. In addition, four graduate students have been partially supported by this fund to pursue academic career, and all of them have passed the qualifying exam towards their PhD degree.

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