ADVANCED MATERIALS

Supporting Information

Anisotropic Thermal Boundary Resistance across 2D Black Phosphorus: Experiment and Atomistic Modeling of Interfacial Energy Transport

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Anisotropic Thermal Boundary Resistance Across Two-Dimensional Black Phosphorous: Experiment and Atomistic Modeling of Interfacial Energy Transport

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Crystal synthesis and orientations

High-quality black phosphorus (BP) crystals were synthesized using the chemical vapor deposition method (see details in the main text of this paper). To identity the crystal orientations, Raman spectra of BP were measured with angel dependence: the A_g^1, A_g^2 peaks are maximized when the polarization is along the AC direction, whereas B_g^2 achieves the highest intensity when the laser polarization forms a 45° angle with the AC direction[S1,S2]. The crystal orientations of BP were also verified by the AB-TDTR[S3] measurement of anisotropic thermal conductivity and show consistency with recent studies[S2,S3].
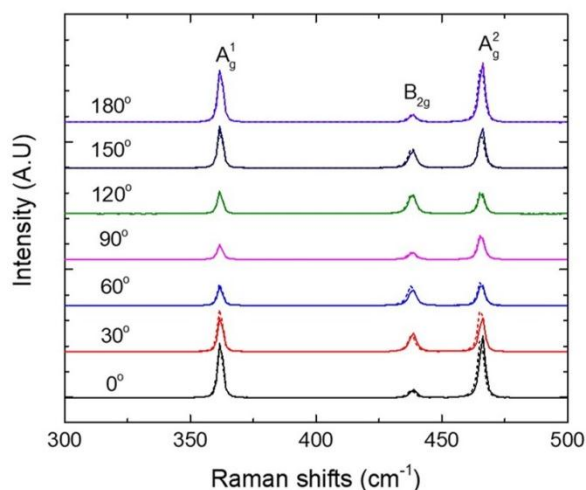

Figure S1. Angle-dependent Raman spectroscopy of BP. Measurement are done for samples with thickness of 1 mm (solid lines) and 50 um (dashed lines), showing agreement.

Sample processing and measurement

We exfoliated the BP crystals to achieve a fresh BP surface and load the sample into vacuum chamber (10^{-7} torr) for metal deposition. Note that for all the thermal measurement in this work, the samples are kept in cryostat (Janis, ST-100H) under a high vacuum ~ 10^{-4} torr to avoid oxidation[S2]. We conducted Energy Dispersive X-ray Spectroscopy (EDS) at the cross-section interface of Al-BP samples (Figure S2). Only Al and P peaks are detected and there is no observation of any impurity. The escape peak (P Si-ESC) at ~ 0.3 keV is generated from the EDS silicon detector crystal.
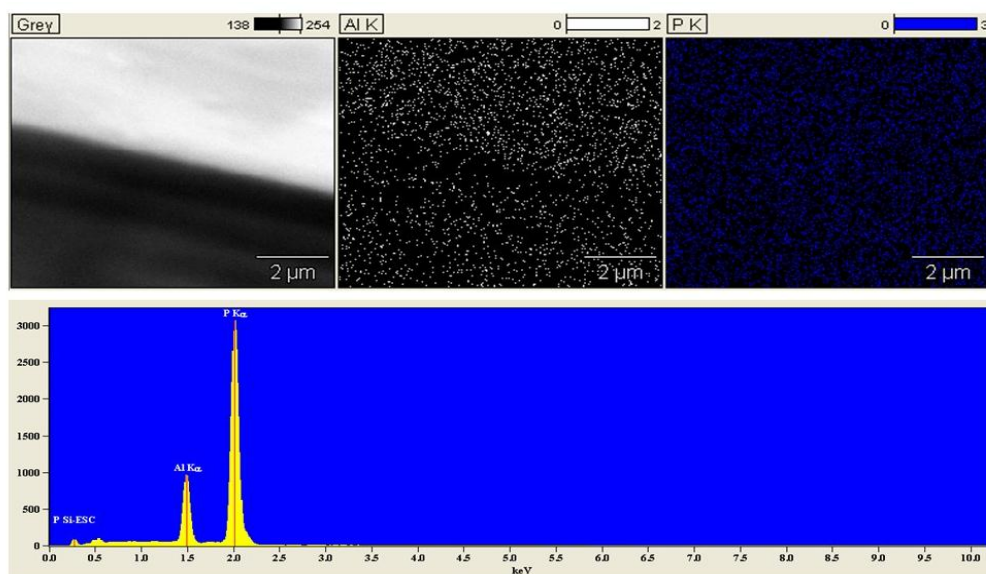

Figure S2. Energy dispersive x-ray spectroscopy (EDS) analysis near the Al-BP interface.

First principle calculations of phonon band structures

To obtain the full phonon dispersion relationships of BP and Al, the second order interatomic force constants are needed for the construction of the dynamical matrix[S9]. We applied the density functional theory (DFT) calculations and finite displacement method to obtain the interatomic force constants corresponding to the equilibrium crystal structures[S9–S11]. For the DFT calculations, we used the open-source package, Quantum Espresso[S12] and XSEDE computational platform[S13] to construct a supercell with a 5×5×2 cubic unit cell for BP and 3×3×3 cubic unit cell for Al with periodic condition and a wave pseudopotential with PBEsol functional[S14,S15] was adopted. The kinetic-energy cut-off for the plane-wave basis set was 550 eV for Al and 960 eV for BP. 10×10×10 and 4×4×4 Monkhorst-Pack meshes were used for the reciprocal space of Al and BP, respectively. The interlayer van de Waals interaction was corrected by using the DFT-D functionals[S16]. The lattice constants for the calculated equilibrium structure of Al and BP were compared with the experimental values[S17–S19] and are in good agreements in Table S1. Under the equilibrium structure, the phonon band structures can be calculated by extracting the second order force constants by displacing the atoms with a finite distance. To verify our calculation results, the calculated phonon dispersion relationships along different directions were compared to experimental data from neutron scattering experiments[S20,S21], showing good consistence in Fig. 3 (a-d).

Table S1. Lattice constants obtained from the DFT calculations and experiments.

Lattice constant (Å)	Aluminum	Black phosphorus
Our DFT calculation	4.013	3.294, 10.424, 4.329
Experiments[S17-S19]	4.046	3.314, 10.478, 4.376

Molecular dynamics simulations

To further quantify TBR between Al and BP along the different crystal directions and phonon mode conversion across branches, we performed the nonequilibrium molecular dynamics (MD) simulations. In the MD simulation, to minimize the lattice mismatch at the interface between BP and Al, the supercells were $60\times5\times12$, $11\times5\times50$ and $11\times20\times12$ for BP and $50\times13\times13$, $9\times13\times50$, $9\times50\times13$ for Al respectively when the interface is normal to the ZZ, AC and c directions. The strain on these three interface systems is below 0.2%. The embedded-atom method empirical potential[S22] was used for describing the interaction between Al atoms. The Stillinger–Weber potential and Lennard-Jones (LJ) potential were adopted for the intra- and inter-plane interactions in BP, respectively[S23–S25]. The interfacial interaction between Al and BP was simulated using LJ potential $V_{ij} = 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right]$, where the ε is the interatomic energy and σ the distance corresponding to the zero potential energy[S24,S25]. The MD simulations were performed with the open source package, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[S26]. The time step was set at 0.5 fs. The systems were relaxed under canonical ensemble at 300 K for 3 ns after a first relaxation under the isothermal–isobaric ensemble (300 K and 0 Pa) for 3 ns. Then the microcanonical ensemble was applied to the system for 4 ns. To ensure a significant temperature drop at the interface and avoid the nonlinear effect[S27], the heat flux was set as ~ 5, 3.5, and 3.3 GW/m^2 for the ZZ, AC, and CP respectively. The heat flux was applied through the system to induce a steady-state temperature gradient for 3 ns. The temperature data in the last 1 ns was sampling for TBR calculation.

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