Supplementary Information

Thermal Properties and Phonon Spectral Characterization of Synthetic Boron Phosphide for High Thermal Conductivity Applications

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Materials and Methods

Chemical synthesis of single crystal boron phosphide (BP)

High quality single crystal BP is synthesized by solution growth method. Stoichiometric ratio of high-purity boron, nickel, and red phosphorus powder (99.99% purity, from Alfa Aesar) are placed into a quartz tube. The quartz tube is evacuated and flame sealed under high vacuum (10^{-5} torr). The quartz tube is placed into the customized reaction furnace and heated up to 1373 K and held on the temperature for 4 days, then slowly cool down to room temperature. The reaction steps are repeated to achieve high quality crystals. After finishing reaction, aqua regia solution is used to purify BP, followed by acetone and isopropanol wash before material characterization and thermal measurement.

TDTR measurement

TDTR method is a reliable standard thermal conductivity measurement technique that has been used to measure thermal conductivity of a wide range of materials. Ti:Sapphire laser with 80MHz repetition rate are split into pump and probe beam by beam splitter. The frequency of pump beam is modulated by electrical optic modulator (EOM). The modulated pump beam heat up the sample surface which create shape temperature rise. The transient temperature decay is monitored by following probe beam which is delayed by mechanical delay stage which gives picosecond resolution of temperature decay. By observing change of reflectance signal by photodetector and lock-in amplifier, thermal conductivity of sample can be extracted. The reflectance signal provides in-phase signal (V_{in}) and out-phase signal (V_{out}). Both amplitude, $\sqrt{V_{in}^2 + V_{out}^2}$, and phase signal, $\tan^{-1}(-\frac{V_{out}}{V_{in}})$, are used to extract thermal properties of BP. Before the measurement, we deposit the 80 nm of Aluminum film on the top of BP for

optical transducer. Sensitivity analysis is performed to optimize the experimental conditions and ensure sufficient measurement sensitivity for the high thermal conductivity measurement from 77K to 298K. In addition, to increase measurement sensitivity of TDTR, we use a two-step TDTR fitting approach. First, we use the amplitude signal to extract thermal interface conductance between Al and BP ($G_{Al\text{-}BP}$) because the amplitude signal is more sensitive than the phase signal to $G_{Al\text{-}BP}$. And then we fix the $G_{Al\text{-}BP}$ value and obtain the BP thermal conductivity by fitting the phase signal.

Details in simulation

The BP spectral volumetric specific heat, group velocity and relaxation times for acoustic branches are obtained from the previous calculation results[1–3]. To be consistent with TDTR experiment, the simulation is performed in the same geometric domain as the experimental condition with time range from 0 to 6 ns. The thickness of the BP is considered as infinite given the sample thickness is much larger than the thermal penetration depth in the transient measurement. The initial temperature distribution in Al film follows the Gaussian distribution $\Delta T = \exp(-2r^2/r_l^2)$, where r_l is the pump beam radius, and $D = 2r_l$ is the pump beam diameter. The temperature in BP is initialized at 300 K. During initialization, phonon bundles are distributed uniformly in a region with a radius of $2r_l$ in Al film, but with different effective energy based on local initial temperature. The top surface of Al film is treated as diffusive adiabatic boundary. Once the phonon touches the diffusive adiabatic boundary, it will be reflected with randomly redistributed direction but unchanged frequency and energy. At the Al-BP interface, the phonon has a probability to be diffusively reflected by or transmitted through the interface and the thermal conductance at the Al-BP interface was set to be consistent with

experimental value: for example, 1.2×10^8 W/(m^2 · K) at 298 K. To calculate the surface temperature as a function of time, a sampling region was defined as $\{(r,z)|r \leq r_l, z \leq 5 \text{ nm}\}$ to represent Al surface. The average phonon energy density of sampling region was counted with time goes on, and then converted into temperature.

To extract the BP thermal conductivity from VRMC result, a Fourier's model treating BP thermal conductivity as a fitting parameter was developed to fit the VRMC result. The initial condition and sampling region of Fourier's model are the same as the VRMC model. The data picked up for fitting are in the time range of 1 ~ 6 ns, and normalized based on the surface temperature at 900 ps.

The time-averaged spectral-dependent flux can be obtained by VRMC. The time-averaged flux contributed by a single phonon bundle during the whole simulation time can be expressed as

$$f = \frac{\varepsilon \sum_{i=1}^{N} \hat{s}_i L_i}{\sum_{i=1}^{N} \tau_i} \qquad \text{(S1)}$$

where ε is the effective energy carried by this phonon bundle, L_i and τ_i are distance and time between two successive scattering events in advection procedure i, and $\hat{s}_i$ is the unit direction vector. If the total simulation time for each phonon bundles are the same, we have $f \propto \varepsilon \sum_{i=1}^{N} \hat{s}_i L_i$. So the cross-plane and in-plane flux contributed by a single phonon bundle during one advection procedure are εL_z and εL_r respectively, where L_z and L_r are projection of L_i to axial and radial direction respectively[4]. During each internal scattering event, the mode of the phonon bundle could be changed. We add the flux contribution to the corresponding phonon mode after each advection step to obtain the spectral-dependent flux. In the end, we normalized the spectral-dependent flux by the phonon mode with smallest MFP which is at the cut-off frequency, since we assume the phonon mode with smallest MFP is not suppressed. To avoid the

influence from the interface dispersion mismatch, we start to count the phonon bundles after their emission from the interface into the BP.

Sampling local pseudotemperature is not required, each phonon bundles can be simulated independently, and the algorithm requires no integration timestep and computational cells[4]. During the internal scattering process, the phonon frequencies are redistributed randomly, following the equilibrium distribution $\frac{D(\omega,p)}{\tau(\omega,p,T_{eq})}e_0^* = \frac{D(\omega,p)}{\tau(\omega,p,T_{eq})}\left(e_{T_{loc}}^{loc} - e_{T_{eq}}^{eq}\right)$, so local pseudotemperature T_{loc} is required in order to get $e_{T_{loc}}^{loc}$. But the e_0^* in eq 1 can be linearized as $e_0^* = e^{loc} - e_{T_{eq}}^{eq} \approx (T_{loc} - T_{eq})\frac{\mathrm{d}e_{T_{eq}}^{eq}}{\mathrm{d}T}$. As $(T_{loc} - T_{eq})$ does not influence the distribution, the phonon bundles can be redistributed based on the distribution $\frac{D(\omega,p)}{\tau(\omega,p,T_{eq})}\frac{\mathrm{d}e_{T_{eq}}^{eq}}{\mathrm{d}T}$, without sampling local pseudotemperature.

Energy-dispersive X-ray spectroscopy (EDS)

EDS analysis were performed on BP samples (Figure S1). Only B 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.

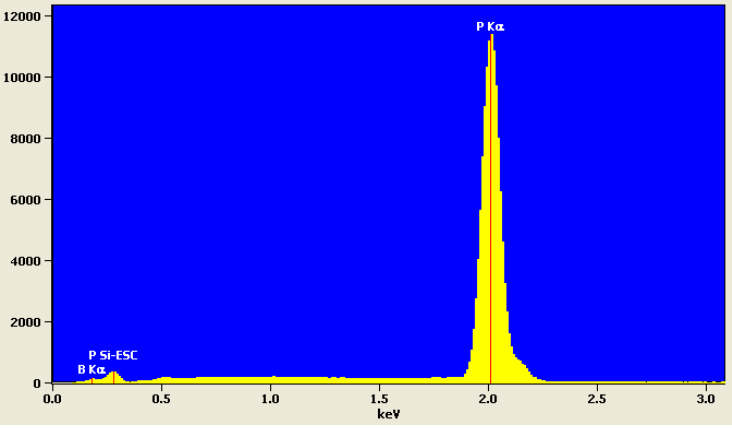

Figure S1. EDS data for single crystal boron phosphide sample.

References

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