SUPPORTING INFORMATION

Hexagonal Boron Nitride-Graphene Heterostructures with Enhanced Interfacial Thermal Conductance for Thermal Management Applications

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Table S1.

Table S2.

S1. Detection of number of graphene and h-BN layers in the samples under study

A. The samples used for the measurements here are comprised of monolayer graphene. Sample sizes vary from $\sim 10\text{-}30\ \mu\text{m}$ which are far larger than the laser spot size ($\sim 1\ \mu\text{m}$). Chain *et al.* reported that the graphene size effect on thermal conductivity is suppressed in supported graphene [1]. The layer number was verified from Raman spectra of the samples at room temperature as shown in original text Figure 2(c). It was observed that the absolute intensities of the G mode were lower than those of the 2D mode in the Raman spectra for all the samples with $I_G/I_{2D} < 0.5$. This has been reported to be a signature of monolayer graphene [2-4]. Figure S1(a) shows the absolute intensities of the G and 2D modes and their relative ratios (which varies in the range of 0.1 to 0.2) for the different samples thus confirming the graphene to be of monolayer thickness. Further, the 2D bands in the Raman Spectra of monolayer graphene has been reported to show single Lorentzian line shape, while multilayer graphene shows a line shape which may be fitted with multiple Lorentzian functions [3]. Figure S1(b) clearly shows that the 2D bands of the graphene flakes in Gr, BG, and BGB (hetero)structures are fitted with single Lorentzian functions, again confirming the graphene flakes to be of monolayer thickness.

Figure S1: (a) Bar diagram showing the absolute intensity of G and 2D Raman modes (left axis) and ratio of intensities of G and 2D mode (right axis). (b) 2D band of graphene in Gr, BG, BGB (hetero)structures.

As has been previously reported, the G and 2D band intensity ratio also depends on charge doping [5] and hence the differential value observed in different samples in use may be due to different extents of unintentional charge doping that may have occurred in the various samples. However, as the intensity ratio values range between 0.10 - 0.20 for our samples, we may safely speculate that the small variations in the unintentional charge doping in the different samples will

not have any consequence on the properties investigated in this work. The following table elaborates the observations and confirms that the graphene in our samples is monolayer.

Table S1: Area under the curve values for G and 2D modes obtained by fitting the room temperature Raman spectra of the related (hetero)structures using Lorentzian functions.

(Hetero)structures	I_G [G mode Area under the curve (unit ²)]	I_{2D} [2D mode Area under the curve (unit ²)]	I_G/I_{2D}
Gr	3243	16073	0.2
BG	1977	18304	0.1
BGB	1909	9519	0.2

B. The thicknesses of the h-BN flakes in the heterostructures were determined from AFM measurements in contact mode (Agilent 5500). It is well known that the thickness of monolayer h-BN is ~ 0.333 nm [6]. The Figure S2 shows the AFM topography image along with the height profile revealing the thickness of the h-BN flakes to be ~ 10 layers [6]. It is worth mentioning that supported 2D layers on a substrate improves their thermal dissipation properties with an increase in the number of layers. Therefore, fabricating a heterostructure (of graphene and h-BN) with multilayer h-BN is expected to improve the thermal performance with respect to the heterostructure with a single h-BN layer.

Figure S2: Left: AFM image showing the topography of h-BN layer. Right: Height profile along the white solid line in the left image.

S2. Determination of laser spot size

In order to determine the laser spot radius, a technique similar to the knife-edge method was employed [7]. A sharp-edged thin strip of gold was deposited on the SiO₂/Si substrate and then a linear Raman mapping was done across the sharp edge of the gold strip in the range of 450 cm⁻¹ to 550 cm⁻¹. The Figure 1(b) shows the linear mapping measurement done. The Raman spectra obtained at the different positions marked (i), (ii), and (iii) are shown and we could clearly observe the disappearance of the Si peak at 520 cm⁻¹ as the laser spot was moved across the sharp gold strip. Figure 1(c) shows the corresponding intensity profile of the Si peak along the linear map. Figure 1(b), the intensity profile was fitted with the function:

$$I(x) = \frac{I_0}{2} \left(1 + \operatorname{erf} \left(\frac{x-x_0}{w_0} \right) \right)$$

The $\frac{dI}{dx}$ for the fitted intensity profile showed a clear Gaussian behaviour and was fitted by the function of type $\exp\left(\frac{-x^2}{r_0^2}\right)$ and hence the spot radius r_0 for 20× (0.94μm) and 50× (0.64μm) objective lenses were determined.

S3. Temperature- and Laser-power-dependence of the Raman spectra

Temperature and power dependent Raman studies were done for all the samples. Figure S3 (a,b) shows the stacks of temperature and power dependent spectra for the different samples. It was observed that all modes show a red-shift with increase in temperature as well as power. This redshift can be attributed to phonon-phonon interaction mediated anharmonic contributions to the interatomic Coulombic potential energy at higher temperatures [8]. The power dependent spectra also show similar red-shifts because the laser-power induces local heating of the sample thereby increasing the temperature near the exposed part of the sample. We have performed laser power dependent experiments in a range from 0.03 mW – 7.15 mW, which results in a huge enhancement in the intensity of the Raman spectra for the various (hetero)structures with increasing laser power thus lowering the noise level in the spectra recorded at higher powers. On the other hand, the temperature-dependent measurements are performed at a fixed laser power (~1 mW). Hence, the signal-to-noise ratio in the temperature-dependent spectra remains almost comparable except at very high temperature say at 450 K. At around 450 K, the adhesive residues that are present on the substrate due to the micromechanical exfoliation process start to evaporate and that often cause a degradation of the counts (or intensity) at high temperatures.

Figure S3: (a) Comparison of temperature-dependent and (b) power-dependent Raman spectra showing the h-BN mode (left) and 2D mode (right) of the different samples. Both the modes show redshift with increase in temperature (and power).

S4: The Optothermal method with calculations and theoretical background

The optothermal method is an easy and non-destructive approach of measuring the thermal conductivity (κ) and interfacial thermal conductance (g) of a material supported on a given substrate, wherein temperature- dependent and power-dependent Raman response is measured. This technique has often been used for the measurement of κ and g of various 2D layered materials [9]. Therefore, we have used this technique for the measurement of κ and g of our samples.

The thermal conductivity (κ), and interface thermal conductance per unit area (g) for the different samples on SiO₂/Si substrate were estimated by using the Raman spectroscopy- based measurement using the approach developed by Cai *et al.* [9]

A 2D-layer when supported on a substrate can dissipate the heat through the in-plane and out-of-plane heat conduction channels, (neglecting the contribution from convection and radiation losses). The temperature distribution in the sample can be obtained from heat diffusion equation in cylindrical coordinates as follows [9-11]

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) - \frac{g}{\kappa l} (T - T_a) + \frac{q}{\kappa} = 0 \quad (1)$$

Here T , T_a , g , κ , l , and q represent the temperature at position r , ambient temperature, interface conductance, thermal conductivity, thickness of the sample, and volumetric heat coefficient respectively. The volumetric optical heating q can be represented as:

$$q = \frac{q_0}{l} \exp \left(-\frac{r^2}{r_0^2} \right) \quad (2)$$

Here q_0 and r_0 represent the peak absorbed laser power per unit area at the centre of the beam spot and the radius of the laser beam spot respectively. The total absorbed laser power Q is then

$$Q = \int_0^\infty q_0 \exp \left(-\frac{r^2}{r_0^2} \right) 2\pi r dr = q_0 \pi r_0^2 \quad (3)$$

Substituting $\theta \equiv (T - T_a)$ and $z = \left(\frac{g}{\kappa l} \right)^{\frac{1}{2}} r$ into equation (1), we get a nonhomogeneous Bessel's equation:

$$\frac{d^2 \theta}{dz^2} + \frac{1}{z} \frac{d\theta}{dz} - \theta = -\frac{q_0}{g} \exp \left(-\frac{z^2}{z_0^2} \right) \quad (4)$$

The solution to equation (4) is given as

$$\theta(z) = C_1 I_0(z) + C_2 K_0(z) + \theta_p(z) \quad (5)$$

where $I_0(z)$ and $K_0(z)$ are the zero-order modified Bessel functions of first and second kind, respectively.

$$\theta_p(z) = I_0(z) \int K_0(z) \frac{\pi q_0}{2g} \exp \left(-\frac{z^2}{z_0^2} \right) dz - K_0(z) \int I_0(z) \frac{\pi q_0}{2g} \exp \left(-\frac{z^2}{z_0^2} \right) dz \quad (6)$$

The boundary conditions $\left(\frac{d\theta}{dz} \right)_{z=0} = 0$ and $\theta(z \rightarrow \infty) = 0$ yield $C_2 = 0$ and $C_1 = -\lim_{z \rightarrow \infty} \left(\frac{\theta_p(z)}{I_0(z)} \right)$, which approach a constant value for large z .

The temperature rise in the sample measured by the Raman laser beam is given by:

$$\theta_m = \frac{\int_0^\infty \theta(r) \exp\left(-\frac{r^2}{r_0^2}\right) r dr}{\int_0^\infty \exp\left(-\frac{r^2}{r_0^2}\right) r dr} \quad (7)$$

We define the measure thermal resistance as $R_m \equiv \frac{\theta_m}{Q}$. On the basis of equations (3) and (7)

$$R_m = \frac{\int_0^\infty \left(-I_0(z) \lim_{z \rightarrow \infty} \frac{\theta_p(z)}{I_0(z)} + \theta_p(z) \right) \exp\left(-\frac{r^2}{r_0^2}\right) r dr}{\int_0^\infty \exp\left(-\frac{r^2}{r_0^2}\right) r dr \int_0^\infty q_0 \exp\left(-\frac{r^2}{r_0^2}\right) 2\pi r dr} \quad (8)$$

For measurements with 50× objective:

$$R_{m(50\times)} = \frac{\int_0^\infty \left(-I_0(z) \lim_{z \rightarrow \infty} \frac{\theta_p(z)}{I_0(z)} + \theta_p(z) \right) \exp\left(-\frac{r^2}{r_1^2}\right) r dr}{\int_0^\infty \exp\left(-\frac{r^2}{r_1^2}\right) r dr \int_0^\infty q_1 \exp\left(-\frac{r^2}{r_1^2}\right) 2\pi r dr} \quad (9)$$

For measurement with 20× objective:

$$R_{m(20\times)} = \frac{\int_0^\infty \left(-I_0(z) \lim_{z \rightarrow \infty} \frac{\theta_p(z)}{I_0(z)} + \theta_p(z) \right) \exp\left(-\frac{r^2}{r_2^2}\right) r dr}{\int_0^\infty \exp\left(-\frac{r^2}{r_2^2}\right) r dr \int_0^\infty q_2 \exp\left(-\frac{r^2}{r_2^2}\right) 2\pi r dr} \quad (10)$$

To avoid the artificial shift in mode frequency we have used $R_m = \frac{\partial \theta_m}{\partial Q}$ instead of $R_m \equiv \frac{\theta_m}{Q}$.

And, R_m depends on κ and g . At a same time, R_m can be experimentally obtained using the following relation

$$R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} \quad (11)$$

Where χ_P and χ_T are first order power and temperature coefficients, [$\chi_P = \left(\frac{d\omega}{dP}\right)_T$ or $=\left(\frac{\partial \omega}{\partial Q}\right)$ and $\chi_T = \left(\frac{d\omega}{dT}\right)_P$ or $=\left(\frac{\partial \omega}{\partial \theta_m}\right)$] respectively.

The R_m values obtained experimentally using equation (11) from the temperature-dependent and power-dependent Raman data for the 50× and 20× objective lenses are used to avoid any calibration error in the κ and g values for the samples by using equation 8. To solve it numerical we have used $R_m = \frac{\partial \theta_m}{\partial Q}$ ratios for 50× and 20× to get accurate results.

Calculations:

(i) For Gr (graphene on SiO₂/Si):

In case of 50× objective

$$\chi_P = -0.993 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.035 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 28.371 \text{ K/mW}$$

In case of 20× objective

$$\chi_P = -0.308 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.009 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 34.222 \text{ K/mW}$$

$$\text{Hence, } R_m \text{ ratio (of 50× to 20×)} = (28.371/34.222) = 0.829$$

The peak absorbed laser power per unit area (q_1) corresponding to 50× objective: $q_1 = \frac{Q_1 \alpha}{\pi r_1^2}$

where,

Q_1 = Total absorbed laser power

r_1 = Laser spot radius for 50× objective = 0.64 μm

α = Optical absorption coefficient of monolayer graphene = 0.023 [9,12]

$$q_1 = \frac{1.38 \times 10^{-3} \times 0.023}{\pi \times (0.64 \times 10^{-6})^2} \text{ W m}^{-2} = 2.46 \times 10^7 \text{ W m}^{-2}$$

Similarly, for the 20× objective the peak absorbed laser power per unit area (q_2): $q_2 = \frac{Q_2 \alpha}{\pi r_2^2}$

where,

Q_2 = Total absorbed laser power

r_2 = Laser spot radius for 20× objective = 0.94 μm

α = Optical absorption coefficient = 0.023

$$q_2 = \frac{2.41 \times 10^{-3} \times 0.023}{\pi \times (0.94 \times 10^{-6})^2} \text{ W m}^{-2} = 1.99 \times 10^7 \text{ W m}^{-2}$$

Thickness (l) of graphene (monolayer) = 0.335 nm.

We have used the information of absorbed power or volumetric heat coefficient ($q_{1,2}$), laser spot radius ($r_{1,2}$), and thickness of the sample (l) in the equation (8) with the respective R_m value of the corresponding objective (50× or 20×) and solved the equation (8) numerically to estimate κ and g by taking the ratio of R_m for 50× to 20×. The estimated values for Gr (graphene on SiO₂/Si) sample are $\kappa = 600.0 \text{ W m}^{-1} \text{ K}^{-1}$ and $g = 1.15 \text{ MW m}^{-2} \text{ K}^{-1}$

(ii) **For BN (h-BN on SiO₂/Si):**

In case of 50× objective

$$\chi_P = -0.052 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.041 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 1.268 \text{ K/mW}$$

In case of 20× objective

$$\chi_P = -0.025 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.034 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 0.735 \text{ K/mW}$$

$$\text{Hence, } R_m \text{ ratio (of 50× to 20×)} = (1.268/0.735) = 1.725$$

Now, the peak absorbed laser power per unit area (q_1) corresponding to for 50× objective: $q_1 = \frac{Q_1 \alpha}{\pi r_1^2}$

where,

Q_1 = Total absorbed laser power

r_1 = Laser spot radius for 50× objective

α = Optical absorption coefficient = $0.015 \times 10 = 0.15$, [12-14]

$$q_1 = \frac{1.38 \times 10^{-3} \times 0.15}{\pi \times (0.64 \times 10^{-6})^2} \text{ W m}^{-2} = 16.08 \times 10^7 \text{ W m}^{-2}$$

Similarly, for 20× objective the peak absorbed laser power per unit area (q_2): $q_2 = \frac{Q_2 \alpha}{\pi r_2^2}$

where,

Q_2 = Total absorbed laser power

r_2 = Laser spot radius for 20× objective

α = Optical absorption coefficient

$$q_2 = \frac{2.41 \times 10^{-3} \times 0.15}{\pi \times (0.94 \times 10^{-6})^2} \text{ W m}^{-2} = 13.02 \times 10^7 \text{ W m}^{-2}$$

Thickness (l) of 10-layer h-BN = 3.4 nm from AFM data discussed in section S1 above.

We have used the above given information of absorbed power or volumetric heat coefficient ($q_{1,2}$), laser spot radius ($r_{1,2}$), and thickness of the sample (l) in the equation (8) with the respective R_m value of the corresponding objective (50× or 20×) and solved the equation (8) numerically to estimate κ and g by taking the ratio of R_m for 50× to 20×. The estimated values for BN (h-BN on SiO₂/Si) sample are $\kappa = 280.0 \text{ W m}^{-1} \text{ K}^{-1}$ and $g = 25.6 \text{ MW m}^{-2} \text{ K}^{-1}$

(iii) **For BG heterostructure (h-BN on graphene on SiO₂/Si):**

In case of 50× objective

$$\chi_P = -0.226 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.022 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 10.272 \text{ K/mW}$$

In case of 20× objective

$$\chi_P = -0.373 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.034 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 10.970 \text{ K/mW}$$

$$\text{Hence, } R_m \text{ ratio (of 50× to 20×)} = (10.272/10.970) = 0.936$$

$$\text{Now, for 50× the peak absorbed laser power per unit area (q}_1\text{): } q_1 = \frac{Q_1 \alpha}{\pi r_1^2}$$

where,

Q_1 = Total absorbed laser power

r_1 = Laser spot radius for 50× objective

α = Optical absorption coefficient = $0.15 + 0.023 = 0.173$ (It is assumed that the net absorption coefficient of the BG heterostructure will be reasonably close to the sum of the two. To note that small differences in the values of absorption coefficient do not significantly affect the overall estimation of the κ and g . Hence, our assumption is reasonably acceptable.) [9,12-14]

$$q_1 = \frac{1.38 \times 10^{-3} \times 0.173}{\pi \times (0.64 \times 10^{-6})^2} \text{ W m}^{-2} = 18.550 \times 10^7 \text{ W m}^{-2}$$

$$\text{Similarly, for 20× the peak absorbed laser power per unit area (q}_2\text{): } q_2 = \frac{Q_2 \alpha}{\pi r_2^2}$$

where,

Q_2 = Total absorbed laser power

r_2 = Laser spot radius for 20× objective

α = Optical absorption coefficient = 0.038

$$q_2 = \frac{2.41 \times 10^{-3} \times 0.173}{\pi \times (0.94 \times 10^{-6})^2} \text{ W m}^{-2} = 15.019 \times 10^7 \text{ W m}^{-2}$$

Thickness (l) of the BG heterostructure = (3.4+0.335) nm = 3.735 nm (It is approximately considered as the sum of the 11 layers: one monolayer of graphene and 10 layers of h-BN).

We have used the information of absorbed power or volumetric heat coefficient ($q_{1,2}$), laser spot radius ($r_{1,2}$), and thickness of the sample (l), as given above, in the equation (8) with the respective R_m value of the corresponding objective (50 $\times$ or 20 $\times$) and solved the equation (8) numerically to estimate κ and g by taking the ratio of R_m for 50 $\times$ to 20 $\times$. The estimated values for BG heterostructure (h-BN on graphene on SiO₂/Si) sample are $\kappa = 1072 \text{ W m}^{-1} \text{ K}^{-1}$ and $g = 26.2 \text{ MW m}^{-2} \text{ K}^{-1}$

(iv) **For BGB heterostructure (h-BN on graphene on h-BN on SiO₂/Si):**

In case of 50 $\times$ objective

$$\chi_P = -0.671 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.098 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 6.840 \text{ K/mW}$$

In case of 20 $\times$ objective

$$\chi_P = -0.437 \text{ cm}^{-1} / \text{mW}$$

$$\chi_T = -0.100 \text{ cm}^{-1} / \text{K}$$

$$\text{Therefore, } R_m = \frac{\partial \theta_m}{\partial Q} = \frac{\partial \omega}{\partial Q} \frac{\partial \theta_m}{\partial \omega} = \chi_P (\chi_T)^{-1} = 4.37 \text{ K/mW}$$

Hence, R_m ratio (of 50 $\times$ to 20 $\times$) = (6.84/4.37) = 1.565

Now, for 50 $\times$ the peak absorbed laser power per unit area (q_1): $q_1 = \frac{Q_1 \alpha}{\pi r_1^2}$

where,

Q_1 = Total absorbed laser power

r_1 = Laser spot radius for 50 $\times$ objective

α = Optical absorption coefficient = 0.15+0.023+0.15 = 0.323 (We have once again assumed that the effective absorption coefficient of the BGB heterostructure will be the sum of the coefficients of the three layers. Further, small differences in the values of absorption coefficient do not significantly affect the overall estimation of the κ and g . Hence, our assumption is reasonably acceptable.) [9,12-14]

$$q_1 = \frac{1.38 \times 10^{-3} \times 0.323}{\pi \times (0.64 \times 10^{-6})^2} \text{ W m}^{-2} = 34.630 \times 10^7 \text{ W m}^{-2}$$

Similarly, for 20× the peak absorbed laser power per unit area (q_2): $q_2 = \frac{Q_2 \alpha}{\pi r_2^2}$

where,

Q_2 = Total absorbed laser power

r_2 = Laser spot radius for 20× objective

α = Optical absorption coefficient = 0.15+0.023+0.15 = 0.053

$$q_2 = \frac{2.41 \times 10^{-3} \times 0.323}{\pi \times (0.94 \times 10^{-6})^2} \text{ W m}^{-2} = 28.04 \times 10^7 \text{ W m}^{-2}$$

Thickness (l) = (3.4+0.335+3.4) nm = 7.135 nm (Sum of the 21 layers, 10 layers of h-BN, one monolayer of graphene, and another 10 layers of h-BN).

We have used the information of absorbed power or volumetric heat coefficient ($q_{1,2}$), laser spot radius ($r_{1,2}$), and thickness of the sample (l), as given above, in the equation (8) with the respective R_m value of the corresponding objective (50× or 20×) and solved the equation (8) numerically to estimate κ and g by taking the ratio of R_m for 50× to 20×. The estimated values for BGB heterostructure (h-BN on graphene on h-BN on SiO₂/Si) sample are $\kappa = 850.0 \text{ W m}^{-1} \text{ K}^{-1}$ and $g = 105 \text{ MW m}^{-2} \text{ K}^{-1}$

S5. Dependence of surface contact area and surface roughness on introducing h-BN

The schematic given below (Figure S4) depicts how roughness of the graphene layer decreases with the increment of the h-BN layer number. From previous reports [15,16], we know that SiO₂/Si has rougher surface than h-BN layer on SiO₂/Si because of the presence of the dangling bonds and corrugations in the SiO₂/Si substrate, whereas the surface of h-BN layer is free from the dragging bonds [15, 16]. Therefore, the contact area between graphene and the substrate increases, thus increasing the heat dissipation channels through the h-BN layer which increases the interfacial thermal conductance per unit area in BGB by a greater extent.

Figure S4: A schematic showing how the roughness seen by graphene varies as an h-BN layer is introduced in the four (hetero)structures samples.

S6. Effect of flake thickness on κ and g

In our work, we have seen an overall improvement in thermal dissipation properties of graphene by using them in conjunction with h-BN as van-der Waals heterostructures. Both the κ (in-plane thermal conductivity) and g (interfacial thermal conductance per unit area) values of the hybrid structures show enhancement. It must be noted that due to the nanoscale thickness of the 2D materials, the dissipation of heat through cross-planar channels can be very strong for supported graphene-based devices. To employ this property of supported devices, it is important to ensure excellent surface contact with the substrate. Thinner flakes are often prone to defects like folding and corrugation, which in turn result in a decreased interfacial thermal conductance. Therefore, it is often preferable to have multilayer flakes in devices to produce better surface contact and higher interfacial thermal conductance. Yuan *et al.* [17] demonstrated an increase in the interfacial thermal conductance in c-Si supported MoS_2 with increasing thickness of

MoS₂ flakes. On the other hand, Jo *et al.* [18] showed an increase in the in-plane thermal conductivity (κ) of suspended h-BN with increase in the h-BN flake thickness. In our heterostructures, we have therefore, used h-BN layers of thickness 3.4 nm (10 layers, which may be still considered in the 2D limit) with monolayer graphene.

S7. Phonon lifetime vs linewidth of Raman modes

The lifetime of a phonon mode is inversely proportional to the FWHM of the mode ($\Gamma \propto \frac{1}{\tau}$) [19]. Figure S5 shows the FWHMs of the 2D mode of the different samples as a function of temperature. Here we observe that the linewidth corresponding to the 2D mode in Gr, BG, and BGB samples follow the trend: Gr > BG > BGB, which implies that the trend for phonon lifetimes is as BGB > BG > Gr. This is consistent with the increasing trend of phonon lifetimes with increasing number of h-BN and graphene interfaces as seen in Figure 6 of main text.

Figure S5: FWHM of the 2D mode as a function of temperature for the different samples.

Table S2. Comparative accounts of thermal conductivity and interface thermal conductance values of developed graphene-based (hetero)structures in the present study with respect to various reports on graphene-based thermal studies.

Structure	Thermal conductivity (κ) in $\text{WK}^{-1}\text{m}^{-1}$	Interface thermal conductance (g) $\text{MWK}^{-1}\text{m}^{-2}$	Method	Supported/ Suspended	Reference
h-BN/SiO ₂ /Si (BN)	280	25.6	Optothermal Raman method (Experiment)	Supported	Present work
Gr/SiO ₂ /Si (Gr)	600	1.15			
h-BN/Gr/SiO ₂ /Si (BG)	1072	26.2			
Gr/h-BN/Gr/SiO ₂ /Si (BGB)	850	105			
Gr/SiO ₂ /Si	5000	-	Optothermal Raman method (Experiment)	Suspended	<i>Nano Letters.</i> 2008 , 8, 902
Gr/SiO ₂ /Si	600	-	Electrical heating (Experiment)	Supported	<i>Science</i> 2010 , 328, 213
Gr/ SiC	-	0.02	Raman thermometry combined with Joule heating (Experiment)	Supported	<i>Small</i> 2011 , 7, 3324
Gr/Au/SiO ₂ /Si	370	28	Optothermal Raman method (Experiment)	Supported	<i>Nano Lett.</i> 2010 , 10, 1645.
Gr/h-BN	1347.3	-	Theoretical prediction	-	<i>Nanotechnology</i> 2017 , 28, 225704
Gr/h-BN	-	6420	Theoretical prediction on lateral heterostructures	-	<i>Nano letters.</i> 2016 , 16, 4954
Gr/h-BN	-	7.4	Raman thermometry combined with Joule heating (Experiment)	Supported	<i>Appl. Phys. Lett.</i> 2014 , 104, 081908

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