

Temperature-Dependent Thermal Boundary Conductance of Monolayer MoS₂ by Raman Thermometry

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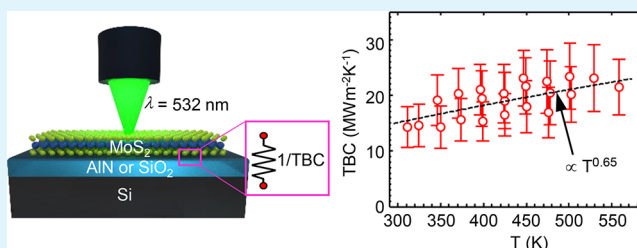
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S Supporting Information

ABSTRACT: The electrical and thermal behavior of nano-scale devices based on two-dimensional (2D) materials is often limited by their contacts and interfaces. Here we report the temperature-dependent thermal boundary conductance (TBC) of monolayer MoS₂ with AlN and SiO₂, using Raman thermometry with laser-induced heating. The temperature-dependent optical absorption of the 2D material is crucial in such experiments, which we characterize here for the first time above room temperature. We obtain TBC $\sim 15 \text{ MW m}^{-2} \text{ K}^{-1}$ near room temperature, increasing as $\sim T^{0.65}$ in the range 300–600 K. The similar TBC of MoS₂ with the two substrates indicates that MoS₂ is the “softer” material with weaker phonon irradiance, and the relatively low TBC signifies that such interfaces present a key bottleneck in energy dissipation from 2D devices. Our approach is needed to correctly perform Raman thermometry of 2D materials, and our findings are key for understanding energy coupling at the nanoscale.

KEYWORDS: thermal boundary conductance (TBC), 2D materials, MoS₂, Raman thermometry, optical absorption, aluminum nitride (AlN), Kapitza length



INTRODUCTION

Thermal interfaces are expected to dominate energy dissipation in 2D semiconductor devices, and their characterization and understanding have become essential.^{1,2} For example, drive currents in state-of-the-art 2D devices are critically limited by their heat dissipation capabilities,^{3,4} which are determined by thermal interfaces.¹ Moreover, understanding the fundamentals of heat flow across interfaces, namely, the thermal boundary conductance (TBC), is an ongoing challenge in the thermal physics of materials and calls for advances in existing experimental techniques.^{5,6}

Among existing techniques, Raman thermometry is attractive to study 2D material thermal interfaces due to its material selectivity. Raman thermometry enables unprecedented (nanometer-scale) resolution along the laser path by simultaneously measuring the temperature of several Raman-active materials, even monolayers like graphene and h-BN.⁷ Yet, characterization of thermal properties requires not only a measurement of the temperature but also an accurate definition of the input power density and a suitable thermal model. With Raman thermometry the temperature is measured optically, but the input power could be either electrical^{1,7–9} or optical.^{10–14} The Joule input power in electrical heating experiments is well-defined, but it requires fabricating high-quality devices that

carry high current densities sufficient to induce measurable Joule heating.¹ These requirements limit the materials and structures that can be used. The optical heating experiment, which simply requires increasing the Raman laser power applied to the sample, can readily be carried out on different materials and stacks. Nevertheless, a challenge of the Raman optical heating experiment is to accurately define the relevant input power and its density. Moreover, it is crucial to understand the heat dissipation mechanism in such experiments, as discussed below.

We previously measured the TBC of monolayer (1L) MoS₂ transistors on SiO₂ by Raman thermometry with direct electrical self-heating (during transistor operation), finding $G = 14 \pm 4 \text{ MW m}^{-2} \text{ K}^{-1}$ near room temperature in exfoliated and chemical vapor deposited (CVD) films.¹ Recently, Yasaie et al.¹⁵ measured a larger value of $G = 26 \pm 7 \text{ MW m}^{-2} \text{ K}^{-1}$, however, by indirect heating across the MoS₂ from a Ti/Au heater on top. These values are within reasonable agreement, given the uncertainties of the measurements. Our previously measured TBC is equivalent to a Kapitza length $L_K \sim 90 \text{ nm}$ of

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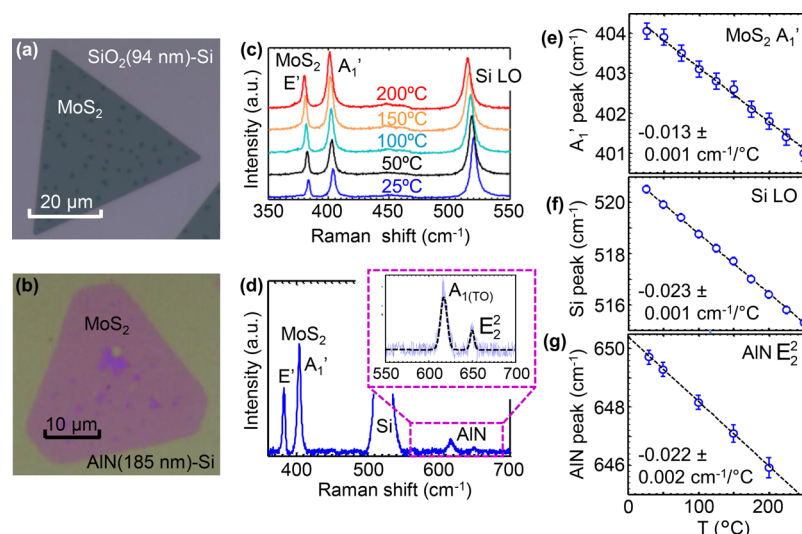


Figure 1. Monolayer MoS₂ Raman and temperature calibration. Optical image of CVD-grown MoS₂ on (a) SiO₂(94 nm)-Si and (b) on AlN(185 nm)-Si showing large triangular crystals and small bilayer spots ($\sim 0.5 \mu\text{m}$ in size). The measurements were carried out only on the 1L MoS₂. (c) T -dependent Raman spectra at varying stage temperatures of the 1L MoS₂ on SiO₂(94 nm)-Si. (d) Simultaneous Raman spectra of MoS₂ on AlN(185 nm) on Si(substrate). The inset shows the AlN peaks, which have a weaker Raman signal compared with the Si and MoS₂. Raman shift vs stage temperature calibration of (e) MoS₂ A₁' peak, (f) the Si substrate peak, and (g) AlN E₂' peak. The absorbed laser power was kept below $20 \mu\text{W}$ in the MoS₂ to avoid measurable laser heating during the calibration.

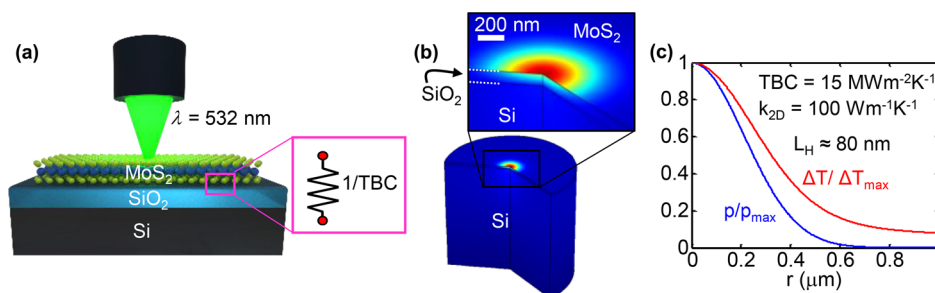


Figure 2. Laser heating experiment and thermal model. (a) Schematic sample structure and measurement setup. The thermal boundary resistance ($=1/\text{TBC}$) at the MoS₂-SiO₂ interface is highlighted. (b) Simulated temperature rise during laser heating in the 2D axisymmetric finite element model. (c) Normalized power density and temperature rise in the MoS₂ film vs radial coordinate for $G = 15 \text{ MW m}^{-2} \text{ K}^{-1}$ and thermal conductivity $k_{2D} = 100 \text{ W m}^{-1} \text{ K}^{-1}$ illustrating a small thermal healing length ($L_H \sim 80 \text{ nm}$) compared to the laser beam size ($r_0 \sim 300 \text{ nm}$). The short L_H results in the insensitivity of the measurement to the thermal conductivity of the 2D material (see Supporting Information, section 2).

SiO₂ (where $k_{\text{SiO}_2} \approx 1.4 \text{ W m}^{-1} \text{ K}^{-1}$) at room temperature, often dominating the thermal resistance of MoS₂ devices.

Here we measure the TBC of monolayer CVD-grown MoS₂ on both SiO₂ and AlN via direct optical heating, as a function of temperature. Both interfaces (MoS₂-SiO₂ and MoS₂-AlN) show very similar values of TBC ($\sim 15 \text{ MW m}^{-2} \text{ K}^{-1}$), in agreement with our electrical heating experiments.¹ MoS₂-AlN-Si test structures highlight the unique material selectivity of the Raman technique, allowing us to simultaneously measure the temperature of all three materials in the stack. In addition, the MoS₂-SiO₂ TBC is found to increase as T^n ($n \sim 0.65$) in the range from 25 to 300 °C. This finding is not unexpected due to the (positive) temperature dependence of the phonon specific heat, but it is in contrast with a previous study that neglected the temperature dependence of the absorption.¹¹ Here we take into account the T -dependent absorption of the MoS₂, reporting it for the first time above room temperature. We also present a thermal model of the laser heating experiment for supported MoS₂, emphasizing that the measurement is sensitive to the TBC but not to the thermal conductivity of the 2D film (k_{2D}) when the lateral thermal

healing length is small compared to the laser spot size. Our findings provide important insights to understand heat transfer across 2D material interfaces, with implications for all optical, electronic, and thermoelectric devices based on such nanomaterials.

RESULTS AND DISCUSSION

Raman and Temperature Calibration. Figure 1 shows the measured MoS₂ films, their Raman spectra, and temperature calibrations. MoS₂ films were directly grown by CVD¹⁶ (see Methods) onto thin SiO₂ (Figure 1a) and AlN¹⁷ (Figure 1b) films on Si substrates. (To the best of our knowledge, this also represents the first demonstration of MoS₂ grown by CVD directly onto AlN.) Section 1 of the Supporting Information includes TBC measurements of exfoliated 1L MoS₂ showing similar results. The optical images in Figure 1a,b show large 1L triangular crystals ($\sim 50 \mu\text{m}$ on SiO₂ and $\sim 30 \mu\text{m}$ on AlN) with small ($\sim 0.5 \mu\text{m}$) bilayer regions.¹⁸ All Raman measurements were carried out on the 1L MoS₂ areas, as verified by their Raman spectra (see ref 1).

The Raman spectra of MoS₂ on SiO₂ vs stage temperature are shown in Figure 1c, and the spectrum of MoS₂ on AlN at room T is shown in Figure 1d. The temperature calibration of peak shift vs stage temperature for MoS₂ A₁', Si longitudinal optical (LO), and AlN E₂' modes, which served as thermometers, are shown in Figure 1e–g. For our AlN film, the weaker E₂' mode is chosen as thermometer, due to its larger measured temperature coefficient ($\chi = 0.022 \text{ cm}^{-1}/^{\circ}\text{C}$, where the mode frequency dependence is $\omega(T) = \omega_0 + \chi T$) compared with the A₁(TO) mode ($\chi < 0.01 \text{ cm}^{-1}/^{\circ}\text{C}$). The laser intensity was kept low ($P_{\text{abs}} < 20 \text{ }\mu\text{W}$) during the calibration to avoid measurable heating by the laser.

Laser Heating. To better understand the heat dissipation in our experiment, we model the laser heating (schematic shown in Figure 2a) using a finite element thermal simulation (with COMSOL Multiphysics). The Fourier heat diffusion equation is solved with cylindrical coordinates (2D axisymmetric configuration) and a Gaussian-shaped beam heat source. The simulated temperature rise in the sample is shown in Figure 2b. The bottom of the substrate is held at ambient temperature (isothermal boundary condition) and other surface boundaries are thermally insulating (adiabatic boundary condition). The thermal properties of the substrate are well-known, including their temperature dependence around room temperature. The thermal conductivity of doped silicon can be expressed as $k_{\text{Si}} \approx 3 \times 10^4/T \text{ W m}^{-1} \text{ K}^{-1}$, the thermal conductivity of SiO₂ is $k_{\text{SiO}_2} \approx \ln(T^{0.52}) - 1.6 \text{ W m}^{-1} \text{ K}^{-1}$ (where T is in Kelvin), and the TBC between the two is $G_{\text{Si-SiO}_2} \approx 600 \text{ MW m}^{-2} \text{ K}^{-1}$ (following refs 1, 19–23). The heating profile is proportional to the laser spot size and the heat is dissipated mostly in the cross-plane direction into the Si substrate, typical for supported films as discussed below.

The Raman laser heating technique was originally developed for bulk materials, where the thermal conductivity could be extracted,²⁴ and was later extended to suspended 2D films.^{10,25} In *suspended* structures, the heat flows radially “in-plane” from the laser spot toward the supported part of the film, where the heat is sunk “cross-plane” (into the substrate). This combination of in-plane and cross-plane heat flow enables extracting both the thermal conductivity of the 2D film ($k_{2\text{D}}$) and the TBC with the supporting substrate. The separation between the two unknown parameters is obtained by varying the laser spot size.¹⁰ By contrast, in *supported* 2D films, typically the lateral thermal healing length is small compared with the laser spot size (see below); thus, the heat flows predominately in the cross-plane direction into the substrate and is therefore primarily sensitive to the TBC of the 2D film with the substrate.

The heat dissipation mechanism can be understood by comparing the heated area (laser spot) with the lateral thermal healing length $L_{\text{H}} = (k_{2\text{D}}t_{2\text{D}}/g)^{1/2}$ (see, e.g., ref 26), where $k_{2\text{D}}$ and $t_{2\text{D}}$ are the thermal conductivity and thickness of the 2D film, respectively, and g is the total thermal conductance to the substrate per unit area. L_{H} quantifies the characteristic length scale over which the heat travels laterally before sinking to the substrate and is on the order of $\sim 80 \text{ nm}$ for 1L MoS₂ on SiO₂(94 nm)–Si (assuming $k_{2\text{D}} \sim 100 \text{ W m}^{-1} \text{ K}^{-1}$,^{11,12,27} $t_{2\text{D}} = 0.615 \text{ nm}$, $g = 5 \text{ MW m}^{-2} \text{ K}^{-1}$), much shorter than the laser spot ($r_0 > \sim 300 \text{ nm}$). This is illustrated in Figure 2c, which compares the simulated input power and the temperature profile in the MoS₂. Section 2 of the Supporting Information shows a similar comparison for different values of TBC and $k_{2\text{D}}$. We therefore set $k_{2\text{D}} = 50 \text{ W m}^{-1} \text{ K}^{-1}$ in our thermal model^{12,27}

and validated that the extracted TBC values were insensitive (within measurement uncertainty) to changes of $k_{2\text{D}}$ in the range $20\text{--}120 \text{ W m}^{-1} \text{ K}^{-1}$. Given these inputs to the finite element thermal model, the MoS₂–SiO₂ TBC remains a single fitting parameter.

We note that the laser spot size dominates the uncertainty of the measurement and it is useful to vary the spot size during the heating experiment by sweeping the z -position of the objective in order to reduce that uncertainty ($\sim 10\%$ in spot radius, equivalent to $\sim 20\%$ in spot area; see the Supporting Information, section 3). The uncertainty in spot size is comparable to the L_{H} , further signifying the insensitivity of the measurement to the in-plane thermal conductivity.

Absorbed Laser Power. The temperature in our experiment is measured by converting the Raman peak shifts during laser heating to temperature, using the calibrations shown in Figure 1. In addition to the temperature measurement, the extraction of TBC requires the characterization of absorbed laser power in the supported MoS₂ film, including its temperature dependence. The absorbed power is obtained here by multiplying the incident laser power by the absorption of a free-standing 1L MoS₂ and by the enhancement factor of the substrate, as discussed below. We note that the optical absorption of MoS₂ as a function of temperature is measured and reported here for the first time over the $25\text{--}300 \text{ }^{\circ}\text{C}$ temperature range.

Due to the strong interferences of multiple light reflections in the 1L MoS₂–SiO₂–Si structure, it is difficult to directly measure the absorption of the supported film. We therefore estimate the absorption of our 1L MoS₂ on SiO₂–Si by multiplying the free-standing 1L MoS₂ absorption by a wavelength-dependent factor, the intensity of the electric field (of the electromagnetic wave of the laser) at the top surface of SiO₂–Si substrate relative to the intensity of the incident electric field (namely, the enhancement factor of the SiO₂–Si stack). The free-standing absorption is obtained by measuring the (T -dependent) absorption of 1L MoS₂ on quartz, where the quartz dielectric function is known (see Methods). The enhancement factor is calculated by the transfer matrix method²⁸ using the refractive indices of the materials in the stack, which are known at room temperature, and we assume that these reflections do not change significantly with T .

Figure 3a displays four selected absorption spectra at selected stage temperatures between 25 and $300 \text{ }^{\circ}\text{C}$. Both A and B excitons red-shift from ~ 1.82 and 1.97 eV to ~ 1.75 and 1.88 eV , respectively. Such red-shifts with increasing temperature are typically found due to reduced overlap in the orbitals forming the bands in the thermally expanded crystals. Figure 3a also shows that the absorption changes significantly near the A and B excitons. The 1L MoS₂ absorption is obtained by averaging over two measured samples at commonly used laser wavelengths of 488, 515, 532, and 633 nm and fitting them to a linear function of T (dashed lines in Figure 3b). It is evident that in green lasers, for instance, the absorption at $250 \text{ }^{\circ}\text{C}$ is increased by $\sim 30\%$ compared with its room temperature value. Overlooking this $\sim 30\%$ increase in the absorbed power can result in an underestimation of the TBC (and thermal conductivity in suspended films) of the 2D material in Raman thermometry experiments. These temperature-dependent absorption results are essential for calculating the absorbed laser power of 1L MoS₂ for Raman thermometry or other optoelectronic applications above room temperature.

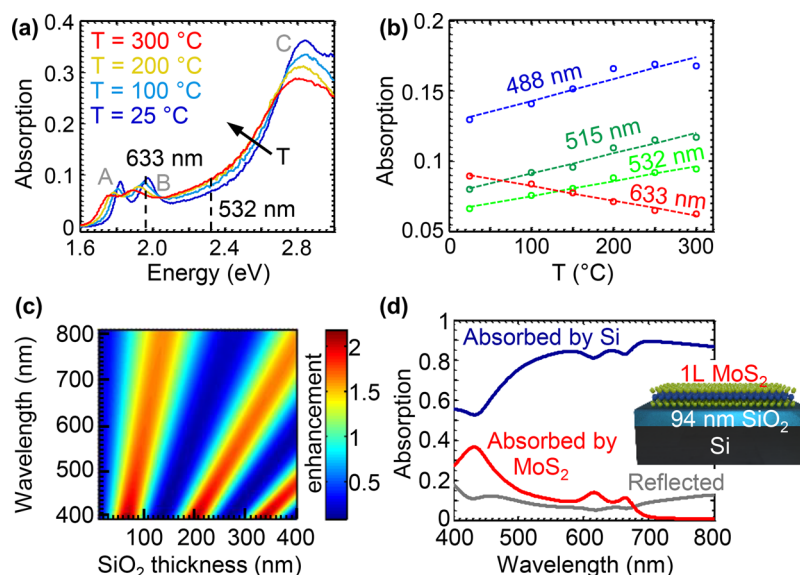


Figure 3. Optical absorption of monolayer MoS₂. (a) Absorption of free-standing 1L MoS₂ vs laser energy at temperatures from 25 to 300 °C. Two typical visible Raman laser lines are indicated by dashed black lines (532 and 633 nm), and the excitonic peaks are labeled. (b) The temperature dependence of optical absorption in free-standing 1L MoS₂ (markers) and linear fits (dashed lines) for typical Raman laser lines: 488, 515, 532, and 633 nm. Note that the absorption can change by more than ~30% between room temperature and ~250 °C. (c) Colormap of the substrate enhancement factor, defined as the intensity of the electric field (on SiO₂-Si substrate) relative to the intensity of the incident electric field for laser wavelengths in the range of 400–800 nm and varying SiO₂ thickness in the range of 10–400 nm. (d) Calculated absorption spectra of 1L MoS₂ on SiO₂(94 nm)-Si (red) and the Si substrate (dark blue) and the fraction of the light reflected (gray). Dielectric functions used for the calculation in part d are taken from ref 29. The absorbed laser power in a supported 2D film is calculated as $P_{\text{abs}} = P_{\text{in}}\alpha_f E$, where P_{in} is the incident laser power, α_f is the absorption of the free-standing film, and E is the enhancement factor of the substrate.

Figure 3c shows the calculated enhancement factor of the SiO₂ (with thickness t_{ox}) on Si substrate, and Figure 3d shows the absorption spectra of 1L MoS₂ and the Si substrate, as well as the reflected light of the MoS₂-SiO₂(94 nm)-Si stack. Most of the laser power is absorbed in the Si substrate (within an absorption depth, here ~0.65 μm at wavelength $\lambda = 532$ nm), heating it above the ambient temperature in spite of its relatively large thermal conductivity (see the Supporting Information, section 4).

Thermal Boundary Conductance and Its Temperature Dependence. Figure 4 summarizes the results of the measured TBC of 1L MoS₂ with SiO₂ and AlN. The temperature rise vs absorbed power in the MoS₂ on SiO₂ (thickness t_{ox}) on Si, with $t_{\text{ox}} = 31$ nm (blue) and 94 nm (red), is shown in Figure 4a. The laser spot size (r_0) is characterized in section 3 of the Supporting Information, and the absorbed power is calculated as described in Figure 3. The error bars in measured temperatures are from the uncertainty in Raman measurement and peak fitting, and the error bars of absorbed power are obtained by propagating error from uncertainty in the three factors mentioned earlier: incident laser power, absorption, and enhancement factor.

The temperature measured by Raman thermometry is defined as follows¹⁰

$$T_m = \frac{\int_0^\infty T(r) e^{-r^2/r_0^2} dr}{\int_0^\infty e^{-r^2/r_0^2} dr} \quad (1)$$

where r_0 is the beam radius. The TBC acts as a single fitting parameter in the thermal model discussed earlier and it is extracted for each measured temperature, given the input power and spot size (for details on the measured beam radius, see the Supporting Information, section 3).

The extracted TBCs are presented in Figure 4b for different MoS₂ temperatures. The stage temperature varied between 25 and 200 °C. The results in Figure 4b include samples with and without a thin AlO_x capping layer (see Methods), showing no measurable difference. The error bars of the TBC are obtained from the uncertainty in the measured thermal resistance, which is a function of the measured temperature, calculated absorbed power, and the measured spot size. The MoS₂-SiO₂ interface accounts for more than 50% of the thermal resistance of the MoS₂-SiO₂(94 nm)-Si stack, and more than 70% for the stack with 31 nm SiO₂. The magnitude and uncertainties of the Si-SiO₂ interface thermal properties^{19,21,23} are small compared with the error bars in our measurement. The MoS₂-SiO₂ TBC shows a weak increase with temperature over the measured range, from 25 to 300 °C. The black dashed line is given by $G = 0.37T^{0.65}$ (in MW m⁻² K⁻¹, with T in K), and the TBC increases by ~40% in the measured temperature range.

We emphasize here the importance of measuring the temperature-dependent absorption of the MoS₂. Section 5 of the Supporting Information shows that the thermal resistance with respect to the incident laser power increases with temperature, which might lead one to conclude that the TBC decreases with increasing temperature,¹¹ a physically unlikely result, as we discuss below. The reason for this apparent increase of the thermal resistance is the increase in absorption of the optical power with temperature (for the 532 nm laser, Figure 3a,b). By taking this effect into account, we find that the thermal resistance with respect to the absorbed power shows a minor decrease with temperature, and hence, the TBC slightly increases with temperature, as shown in Figure 4b.

The TBC typically follows the temperature dependence of the specific heat, which at low temperatures ($T \ll \Theta_D$, where Θ_D is the lower Debye temperature of the two materials

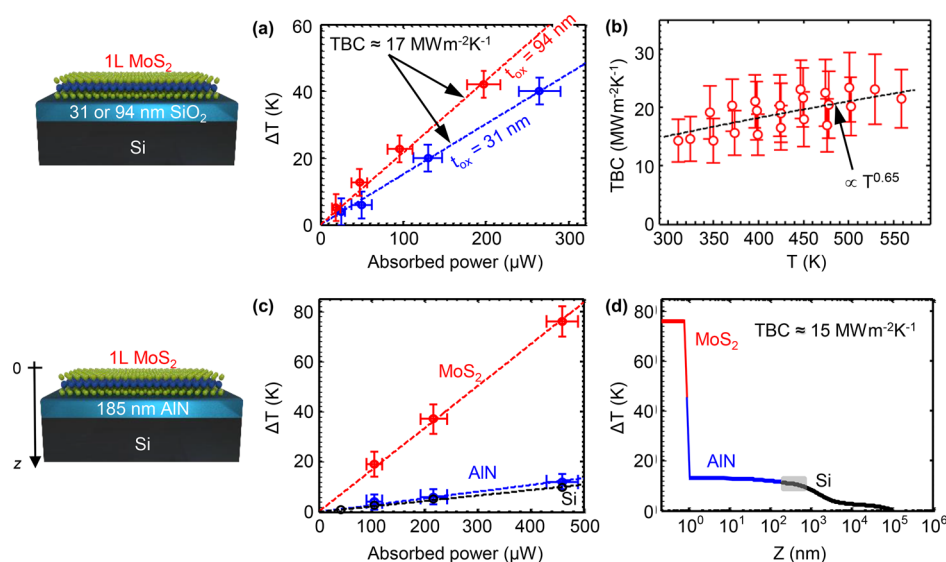


Figure 4. TBC of monolayer MoS₂ and its temperature dependence. (a) Measured temperature rise of 1L MoS₂ on 31 nm (blue) and 94 nm (red) SiO₂ on Si substrate vs absorbed laser power. Calculated absorbed power takes into account the measured temperature-dependent absorption of MoS₂ (Figure 3a,b) and reflections from the substrate, given the exact oxide thicknesses (Figure 3c). Slope of the dashed lines is the thermal resistance of each sample. (b) Measured TBC vs MoS₂ temperature, weakly increasing up to ~600 K. The extracted MoS₂–SiO₂ TBC is 17 ± 5 MW m⁻² K⁻¹ (averaged between 300 and 400 K) and the dashed black line shows T^n dependence with $n = 0.65$. (c) Measured temperature rise of MoS₂ (red) on AlN (blue) and Si (black) as a function of the absorbed power in the MoS₂. The temperature of each material in the stack is measured independently by its Raman signal. The temperature rise of the Si is due to the absorbed power in the Si (see Figure 3d and Supporting Information, section 4). (d) Simulated temperature rise (Gaussian weighted across laser spot size) in the sample along the z-axis, at an absorbed power of 480 μW. The gray area represents the absorption depth of the highly doped Si substrate, where the Si temperature is measured (and where power is absorbed). The extracted MoS₂–AlN TBC is 15 ± 4 MW m⁻² K⁻¹ (averaged between 300 and 400 K) and the estimated thermal conductivity of the AlN film is $k_{\text{AlN}} = 60 \pm 15$ W m⁻¹ K⁻¹.

forming the interface) takes the form $\propto T^{d/m}$, where d is the dimensionality of the material with phonon dispersion $\omega \sim q^m$, q being the phonon wavevector (see ref 2). At high temperatures ($T > \Theta_D$) the specific heat approaches a constant, and the TBC likewise is expected to saturate. Thus, at intermediate temperatures, in the transition between these two regimes, the TBC can be expected to increase more weakly, as $\propto T^n$ (where $0 \leq n < d/m$).^{5,30} In the case of 2D materials, the graphene–SiO₂ TBC was studied in the range from 50 to 500 K and showed an increase with T up to ~300 K, where the TBC saturates.^{31,32} In light of the higher Θ_D of graphene^{33,34} than MoS₂ we expect that the TBC of MoS₂–SiO₂ should have a weak temperature dependence for intermediate temperatures as well, which is what we observe experimentally (Figure 4b).

We also examined the TBC of monolayer MoS₂ with AlN, as shown in Figure 4c,d. The crystalline AlN layer has a measurable Raman signal, whose temperature dependence can be calibrated, as shown in Figure 1d,g. The absorbed power in the MoS₂ is obtained as outlined earlier, with the relevant enhancement factor calculated for the AlN(185 nm)–Si stack (Supporting Information, section 6). The measured temperatures of the MoS₂ (red), AlN (blue), and Si (black) in the Raman laser heating experiment are shown in Figure 4c as a function of the absorbed power in the MoS₂ film.

The differential temperature measurement of all three materials in the stack allows us to estimate the MoS₂–AlN TBC as well as the thermal conductivity of the AlN film. In this case, the MoS₂–AlN TBC is obtained from the temperature difference across the interface and k_{AlN} is obtained from the AlN temperature (see the note in next paragraph on the AlN–Si TBC). This emphasizes the exceptional capability of the Raman technique to measure thermal interfaces without prior knowl-

edge of the thermal properties of the materials in the stack, thanks to its material selectivity. The dashed lines in Figure 4c represent the thermal resistance of MoS₂ and AlN in the laser heating experiment calculated from the model presented in Figure 2, with TBC = 15 MW m⁻² K⁻¹ and $k_{\text{AlN}} = 60$ W m⁻¹ K⁻¹ (averaged between 300 and 400 K) with a laser spot radius of $r_0 = 200$ nm (measured for the objective used in this experiment, magnification 100×, NA = 0.9). The simulated temperature profile along the z-axis when the absorbed power in the MoS₂ is $P_{\text{abs,MoS}_2} = 480$ μW is shown in Figure 4d.

We note that the temperature rise in the Si is not due to the absorbed power in the MoS₂, but rather due to the power absorbed by Si itself ($P_{\text{abs,Si}} = 6.2$ mW) within its absorption depth of ~0.65 μm at the 532 nm laser wavelength³⁵ (gray area in Figure 4d). In the Si substrate, both the absorbed power (heating) and the Raman signal (measured ΔT) originate from the Si surface. The absorbed power decays exponentially with the absorption depth, whereas the substrate is 500 μm thick. The uncertainty in the measured thermal conductivity of the AlN is relatively large, since its temperature rise is low relative to the uncertainty in Raman temperature measurement. Yet the measured thermal resistance is dominated by the MoS₂–AlN TBC, and therefore, the uncertainty in the measured TBC is comparable to the one measured in MoS₂–SiO₂, in spite of the relatively large error in the measured k_{AlN} . The simulated temperature profile shown in Figure 4d is insensitive (<3% error) to the AlN–Si TBC (in the range TBC > 10 MW m⁻² K⁻¹), since the AlN is mostly heated by the Si substrate in this case.

An important result presented in Figure 4 is that the measured TBCs between monolayer, CVD-grown MoS₂, and two different materials, (1) amorphous SiO₂ and (2) crystalline

AlN, are very similar. It is interesting to note that the TBC between 1L MoS₂ and hBN also showed similar values ($\sim 17 \text{ MW m}^{-2} \text{ K}^{-1}$) in a recent study.³⁶ Furthermore, the measured TBC values of MoS₂–SiO₂ and MoS₂–sapphire interfaces reported in ref 15 are within a comparable range. These findings suggest that the TBC is dominated by the material with the weaker energy irradiance across the interface (here MoS₂), as was recently proposed in ref 5. The energy irradiance is proportional to the specific heat and (cross-plane) carrier velocity and is expected to be lower in MoS₂ compared with hBN, AlN, and SiO₂.^{37–39} (We note that the top few nm of our AlN film could be oxidized during MoS₂ growth, forming AlO_xN_y at the interface with MoS₂.)

The lower value of the TBC obtained here and in ref 1 (by direct optical or electrical heating of the MoS₂) compared with the TBC reported in ref 15 (the MoS₂ being heated indirectly by a metal on top) could be due to an “internal thermal resistance”^{40–42} between high-frequency optical phonon (OP) modes and low-frequency modes. If the TBC is dominated by low-frequency modes, the interfacial thermal transport has two main contributions: (i) an internal thermal resistance between the OP modes that are excited (electrically or optically) and the low-frequency modes and (ii) an external thermal resistance between the low-frequency modes in the MoS₂ and the substrate. An indirect heating experiment probes only the latter (external) contribution to the thermal resistance, while the result obtained here, in a direct heating experiment, is the relevant one for devices where the power is dissipated within the MoS₂ film or device.

The Raman thermometry method with optical heating can also be applied, in principle, to multilayer (ML) films, if the temperature-dependent absorption and Raman shifts of the specific ML can be determined. We can also estimate the internal TBC between individual layers of a bulk (or thick ML) film, by normalizing the cross-plane bulk thermal conductivity of MoS₂ ($\sim 2 \text{ W/m/K}$)⁴³ by the layer thickness ($\sim 0.615 \text{ nm}$). The internal TBC between MoS₂ layers is thus $\sim 3 \text{ GW m}^{-2} \text{ K}^{-1}$, two orders of magnitude higher than the TBC with the substrate (for comparison, the interlayer thermal conductance of bulk graphite² is $\sim 18 \text{ GW m}^{-2} \text{ K}^{-1}$). In other words, the MoS₂–SiO₂ TBC is equivalent to ~ 200 layers, or a Kapitza length corresponding to $\sim 130 \text{ nm}$ thick bulk MoS₂. However, in thinner MoS₂ films quasi-ballistic cross-plane transport effects³⁷ must be considered to properly account for the interplay of the TBC and that of the internal thermal resistance, which could be the subject of future work.

CONCLUSIONS

In summary, we measured the temperature-dependent TBC of 1L MoS₂–SiO₂, and the TBC of MoS₂–AlN by Raman thermometry with optical heating. We identified some critical points in the analysis of the laser heating experiment: (1) understanding the heat dissipation that is dominated by cross-plane transport across the interface and (2) characterization of the absorbed power density, including measurement of the T -dependent absorption and measurement of the laser spot size at varying offsets of the focal plane. Near room temperature, we obtain similar values of the 1L MoS₂–SiO₂ TBC as previously measured by electrical heating, equivalent to a Kapitza length of $\sim 90 \text{ nm}$ SiO₂. Knowledge of the T -dependent absorption $\alpha(T)$ is essential to extract the correct T -dependent thermal properties in such optical heating experiments. Taking into account the measured $\alpha(T)$, we find that the TBC weakly

increases with temperature in the range 25–300 °C, in contrast to a previous study.¹¹

We characterized the TBC of MoS₂–AlN by leveraging the simultaneous temperature measurement of all three materials in the stack (MoS₂–AlN–Si), as uniquely enabled by the Raman technique. The obtained MoS₂–AlN TBC is similar to that of the 1L MoS₂–SiO₂ measured here and 1L MoS₂–hBN measured in an earlier study,³⁶ suggesting that the TBC of these interfaces is limited by the MoS₂, which has lower (cross-plane) Debye temperature and phonon irradiance. Our findings are essential to interpret Raman thermometry experiments and to understand the heat dissipation in all optoelectronic devices based on 2D materials.

METHODS

Material Growth. We study monolayer MoS₂ grown by CVD on SiO₂ ($t_{\text{ox}} = 31$ or 94 nm), as well as AlN (185 nm), both on Si substrates (p^+ , electrical resistivity of $1\text{--}5 \text{ m}\Omega \text{ cm}$). A subset of the MoS₂–SiO₂ (94 nm)–Si samples were capped by $\sim 15 \text{ nm}$ AlO_x, as described in ref 1. More details can be found in ref 16. The 185 nm thick AlN was grown by MOCVD on the Si substrate immediately after an HF dip to remove the native oxide. The dislocation density in the AlN film is expected to be $\sim 10^9 \text{ cm}^{-2}$ due to the lattice mismatch and polarity difference.¹⁷ The MoS₂ was deposited by CVD at $850 \text{ }^\circ\text{C}$ directly on the AlN, in a process similar to the one described in refs 16 and 18.

Characterization. Raman spectroscopy was carried out using a Horiba LabRam Revolution HR instrument with a 532 nm laser, 1800 l/mm grating, and two different objectives: a $100\times$ long working distance (LWD) objective with numerical aperture $\text{NA} = 0.6$ and a $100\times$ objective with $\text{NA} = 0.9$. Temperature calibration was done with a Linkam THMS600 stage in ambient air. The peak position of each Raman mode was fitted to a single Lorentzian line shape. After calibrating Raman peak shifts vs temperature on a hot stage (Figure 1), we increase the applied laser power, and the MoS₂ temperature was measured by converting the Raman peak shifts (of MoS₂, Si, and AlN) to temperature rise (the measured temperature is a weighted Gaussian across the laser spot).¹⁰

The absorption of CVD-grown 1L MoS₂ on a quartz substrate was measured at temperatures from 25 up to $300 \text{ }^\circ\text{C}$ in the Linkam THMS600 stage. We studied two samples for all temperatures and calculated the absorption spectra of free-standing 1L MoS₂ from these measurements.^{44–46}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b11641.

Sections detailing the TBC of exfoliated MoS₂, the sensitivity of laser heating to thermal conductivity of supported 2D film, the laser spot, the heating by absorbed power in Si substrate, the thermal resistance of incident vs absorbed power, and the enhancement factor of AlN–Si substrate (PDF)

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Notes

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