Supporting Information

Energy Transport State Resolved Raman for Probing Interface Energy Transport and Hot Carrier Diffusion in Few-Layered MoS_2

Pengyu Yuan[1, ‡], Ridong Wang[1, ‡], Hong Tan[2], Tianyu Wang[1], Xinwei Wang[1,*]

[1] Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA.

[2] School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China.

‡: Equal contribution authors.

*E-mail: xwang3@iastate.edu

S1. Physical model details for picosecond Raman

In the pico-second Raman (zero-transport state), we apply a ps laser (repetition rate is 48.2 MHz, the pulse duration is 13 ps) under 50× (NA=0.5) objective with r_0 as 0.531 μm (1/e peak value) with the same wavelength as the CW laser to focus on the sample to do localized heating and Raman experiment. Using the same wavelength for the two laser sources ensures that the samples have the same laser absorption level in two heating states. In the same way, we obtain the RSC for this ps laser heating case: $\chi_{ps}=\partial\omega/\partial P$. The collected Raman signal reflects the Raman signal-weighted temperature rise during ps laser heating. Within this very short heating time (13

ps), the thermal diffusion length (L_t) for MoS_2 and c-Si is only around 38 nm and 68 nm, respectively. ($L_t = 2\sqrt{\alpha_k t_0}$, α_k=2.75×10^{-5} m^2/s for MoS_2 and 8.92×10^{-5} m^2/s for Si, is the in-plane thermal diffusivity; t_0=13 ps, is the ps laser pulse width). They are much smaller than the laser spot size (r_0=0.53 μm). So we could neglect the heat conduction from the heating region. Besides, the thermal relaxation time of the MoS_2 nanosheets for our interface structure (R is in the order of 10^{-7} K·m^2/W) is estimated to be around 1.9 ns (=$\delta z \cdot \rho c_p R$. δz takes 10 nm, is the thickness of MoS_2 nanosheets; ρc_p=1.89 MJ/m^{3}K, is the volumetric heat capacity, R takes 10^{-7} K·m^2/W, is the interface thermal resistance.) which is much longer than the heating time (13 ps) and much shorter than the laser cooling time (20.8 ns). Therefore, during ps laser heating, the energy absorbed in MoS_2 is used to heat up the sample, but is not transferred out of the heating region to other MoS_2 region or the substrate. Also the sample will be fully cooled to the ambient temperature during the pulse interval. This ensures the RSC measured during ps laser heating has no DC accumulation effect from previous pulses. In summary, the RSC (χ_{ps}) is mainly coming from the volumetric heat capacity of the sample (ρc_p). D and R have an extremely limited contribution to the temperature rise so that we could use this heating state to distinguish the roles of ρc_p and (R, D).

While evaluating the above different states, we do not consider the heat loss to the environment during the Raman measurement in atmospheric condition. This is because, as has been studied for the supported 2D material, the heat loss through radiation or natural convection is negligible compared to the interfacial heat flux.[1] In our steady-state experiment, the measured RSC is proportional to the temperature rise of the two materials, which is a Raman/laser intensity weighted average over the laser spot size as

$$\overline{T}_{\mathrm{CW}} = \int_0^{V_0} I_a(\boldsymbol{r}) T(\boldsymbol{r}) dv \,/\, \int_0^{V_0} I_a(\boldsymbol{r}) dv \,. \tag{S1}$$

For the zero-transport state, the measured temperature rise includes both time and space averaged over the pulse width and heating domain as

$$\overline{T}_{\mathrm{ps}} = \int_0^{t_0} \int_0^{V_0} I_a(\boldsymbol{r},t) T(\boldsymbol{r},t) dv \,/\, \int_0^{t_0} \int_0^{V_0} I_a(\boldsymbol{r},t) dv \,. \tag{S2}$$

S2. Data Reduction details

When a laser beam irradiates the sample surface, multiple reflections happen at the interface between MoS_2 and c-Si as shown in Figure 6(b). Based on the optical properties of these two materials and the Transfer Matrix Method (TMM),[2] we could determine the transmitted power at the top surface (I_{01}), the reflected power at the bottom surface (I_{02}) of MoS_2 and the transmitted power in c-Si top surface (I_{03}). Our method could eliminate the errors from the local laser absorption evaluation and temperature coefficient calibration. We have following detailed explanations.

The temperature coefficient χ_{T} for MoS_2 and c-Si is unknown in our work. For steady-state Raman, the temperature rise (K/mW) of MoS_2 is from two parts: ΔT_1 by the direct laser energy absorption and ΔT_2 by the thermal energy absorption in c-Si. So we express the temperature rise by RSC as

$$\chi_{\mathrm{CW,\,MoS_2}} = (\Delta T_1 + \Delta T_2) \times \chi_{\mathrm{T,\,MoS_2}} \,. \tag{S3}$$

We have $\Delta T_1 \propto (I_{01} + I_{02})$ and $\Delta T_2 \propto I_{03}$. Similar to MoS_2, the temperature rise (K/mW) of c-Si

is also from two parts: ΔT_3 by thermal energy absorption in MoS_2 and ΔT_4 by the direct laser energy absorption in c-Si. It could be represented by RSC as

$$\chi_{\mathrm{CW,\,Si}}=(\Delta T_3+\Delta T_4)\times\chi_{\mathrm{T,\,Si}}. \tag{S4}$$

We also have $\Delta T_3 \propto (I_{01}+I_{02})$ and $\Delta T_4 \propto I_{03}$.

For the zero-transport state ps laser Raman, it is simpler. Only laser absorption happens (the fast thermalization process), and there is no heat conduction. So we could express the temperature rise (K/mW) of MoS_2 and c-Si by RSC as

$$\chi_{\mathrm{ps,\,MoS_2}}=\Delta T_5\times\chi_{\mathrm{T,\,MoS_2}}, \tag{S5}$$

$$\chi_{\mathrm{ps,\,Si}}=\Delta T_6\times\chi_{\mathrm{T,\,Si}}, \tag{S6}$$

where $\Delta T_5 \propto (I_{01}+I_{02})$ and $\Delta T_6 \propto I_{03}$.

From the 3D simulation, for the steady-state CW laser heating, we could get ΔT_1 and ΔT_3 by setting zero absorption in c-Si, ΔT_2 and ΔT_4 by setting zero absorption in MoS_2. From zero-transport state ps laser heating, we could directly get ΔT_5 and ΔT_6 by only considering the laser absorption.

From Eqs. (S3) and (S5), we express the normalized RSC of MoS_2 measured in the experiment as

$$\Theta_{\mathrm{MoS_2}}=\frac{\chi_{\mathrm{CW,\,MoS_2}}}{\chi_{\mathrm{ps,\,MoS_2}}}=\frac{\Delta T_1}{\Delta T_5}+\frac{\Delta T_2}{\Delta T_5}. \tag{S7}$$

From Eqs. (S4) and (S6), we express the normalized RSC of c-Si as

$$\Theta_{\mathrm{Si}} = \frac{\chi_{\mathrm{CW,\,Si}}}{\chi_{\mathrm{ps,\,Si}}} = \frac{\Delta T_3}{\Delta T_6} + \frac{\Delta T_4}{\Delta T_6}. \tag{S8}$$

The temperature rises ΔT_1, ΔT_2, ΔT_3, ΔT_5, and ΔT_6 are only related to the laser absorption in two materials. Additionally, we have $(\Delta T_2/\Delta T_5) \propto [I_{03}/(I_{01}+I_{02})]$ and $(\Delta T_3/\Delta T_6) \propto [(I_{01}+I_{02})/I_{03}]$. To eliminate the laser absorption effect, we multiply these two temperature rise ratios from Eqs. (S7) and (S8) as

$$\Theta_{\mathrm{MoS_2}} = \frac{\Delta T_1}{\Delta T_5} + \frac{(\Delta T_2/\Delta T_5)\times(\Delta T_3/\Delta T_6)}{\Theta_{\mathrm{Si}} - \Delta T_4/\Delta T_6}. \tag{S9}$$

In Eq. (S9), term $\Delta T_1/\Delta T_5$ is not affected by laser absorption rate because both ΔT_1 and ΔT_5 are proportional to (I_{01}+I_{02}). Similarly, term $\Delta T_4/\Delta T_6$ also has nothing to do with laser absorption rate because both ΔT_4 and ΔT_6 are proportional to I_{03}. So the normalized RSC value is now only a function of two parameters: $\Theta(R, D)$, the effect from laser absorption evaluation is successfully ruled out.

S3. ET-Raman experiment results summary

Yim *et al.* have studied the thickness dependent bandgap of MoS_2 nanosheets.[3] The change in the band structure with layer number is due to quantum confinement and the resulting change in hybridization between *pz* orbitals and S atoms and *d* orbitals on Mo atom.[4] We fit the E_g values for different thickness samples by an exponential function

$[E_g(\text{eV}) = 0.5836 \times \exp(-\text{thickness}/3.525) + 1.29]$ and extract the E_g values for our samples as shown in Table S1.

Table S1. Summary of Raman experiment results of seven MoS_2 samples. The thickness dependent bandgap is extracted from Yim *et al.*'s work.[3] The steady-state Raman shift power coefficient (RSC) values under 20× and 100× objective with CW laser (χ_{CW1} and χ_{CW2}) for E^1_{2g} mode of MoS_2 and c-Si. The zero-transport state RSC values under 50× objective with ps laser (χ_{ps}). Also the normalized RSC (Θ_1 and Θ_2).

Sample thickness	Band gap	Raman mode	χ_{CW1} (cm^{-1}/mW)	χ_{CW2} (cm^{-1}/mW)	χ_{ps} (cm^{-1}/mW)	Θ_1	Θ_2
6.6 nm	1.38	E^1_{2g} of MoS_2	$-(0.026\pm1.1\times10^{-3})$	$-(0.150\pm6.5\times10^{-3})$	$-(0.181\pm6.3\times10^{-3})$	$-(0.145\pm8.1\times10^{-3})$	$-(0.829\pm4.6\times10^{-2})$
		c-Si	$-(0.008\pm2.8\times10^{-4})$	$-(0.029\pm1.8\times10^{-3})$	$-(0.057\pm1.8\times10^{-3})$	$-(0.136\pm6.6\times10^{-3})$	$-(0.513\pm3.5\times10^{-2})$
7.8 nm	1.35	E^1_{2g} of MoS_2	$-(0.034\pm1.5\times10^{-3})$	$-(0.171\pm9.5\times10^{-3})$	$-(0.203\pm8.5\times10^{-3})$	$-(0.169\pm1.0\times10^{-2})$	$-(0.841\pm5.9\times10^{-2})$
		c-Si	$-(0.008\pm3.6\times10^{-4})$	$-(0.027\pm1.5\times10^{-3})$	$-(0.051\pm2.2\times10^{-3})$	$-(0.151\pm9.6\times10^{-3})$	$-(0.531\pm3.8\times10^{-2})$
9.6 nm	1.33	E^1_{2g} of MoS_2	$-(0.030\pm1.0\times10^{-3})$	$-(0.158\pm6.4\times10^{-3})$	$-(0.193\pm6.4\times10^{-3})$	$-(0.157\pm7.4\times10^{-3})$	$-(0.818\pm4.3\times10^{-2})$
		c-Si	$-(0.009\pm1.1\times10^{-4})$	$-(0.027\pm1.2\times10^{-3})$	$-(0.050\pm1.2\times10^{-3})$	$-(0.166\pm4.2\times10^{-3})$	$-(0.523\pm2.6\times10^{-2})$
12.0 nm	1.31	E^1_{2g} of MoS_2	$-(0.040\pm1.5\times10^{-3})$	$-(0.187\pm6.6\times10^{-3})$	$-(0.197\pm7.9\times10^{-3})$	$-(0.204\pm1.1\times10^{-2})$	$-(0.947\pm5.1\times10^{-2})$
		c-Si	$-(0.009\pm2.8\times10^{-4})$	$-(0.029\pm6.2\times10^{-4})$	$-(0.056\pm2.9\times10^{-3})$	$-(0.157\pm9.6\times10^{-3})$	$-(0.517\pm2.9\times10^{-2})$
13.2 nm	1.30	E^1_{2g} of MoS_2	$-(0.033\pm1.3\times10^{-3})$	$-(0.175\pm8.3\times10^{-3})$	$-(0.187\pm6.0\times10^{-3})$	$-(0.175\pm9.1\times10^{-3})$	$-(0.935\pm5.4\times10^{-2})$
		c-Si	$-(0.008\pm3.8\times10^{-4})$	$-(0.025\pm1.0\times10^{-3})$	$-(0.059\pm3.2\times10^{-3})$	$-(0.141\pm9.9\times10^{-3})$	$-(0.430\pm2.9\times10^{-2})$
15.6 nm	1.30	E^1_{2g} of MoS_2	$-(0.040\pm1.1\times10^{-3})$	$-(0.189\pm7.7\times10^{-3})$	$-(0.201\pm5.6\times10^{-3})$	$-(0.197\pm7.9\times10^{-3})$	$-(0.940\pm4.6\times10^{-2})$
		c-Si	$-(0.008\pm5.3\times10^{-4})$	$-(0.026\pm8.7\times10^{-4})$	$-(0.050\pm2.7\times10^{-3})$	$-(0.164\pm1.4\times10^{-2})$	$-(0.514\pm3.2\times10^{-2})$
17.4 nm	1.30	E^1_{2g} of MoS_2	$-(0.045\pm2.2\times10^{-3})$	$-(0.217\pm9.4\times10^{-3})$	$-(0.210\pm4.5\times10^{-3})$	$-(0.212\pm1.1\times10^{-2})$	$-(1.03\pm5.0\times10^{-2})$
		c-Si	$-(0.006\pm1.7\times10^{-4})$	$-(0.021\pm7.8\times10^{-4})$	$-(0.054\pm1.2\times10^{-3})$	$-(0.114\pm4.0\times10^{-3})$	$-(0.386\pm1.7\times10^{-2})$

S4. Laser pulse accumulation effect from substrate

For the pulsed laser (ps laser) heating, the temperature rise of the sample is from a single pulse and the steady-state accumulation of the heat. In our experiment, the time (t_c) between pulses from ps laser is around 20.8 ns as shown in Fig. 1(e). Moreover, compared to SiO_2 substrate, c-Si has a larger thermal conductivity and therefore could dissipate the heat more efficiently.[5] Besides, the thermal diffusion length (L_t) in c-Si within one repetition period could be estimated as $L_t = 2\sqrt{\alpha_k t_c} = 2.71\ \mu m$, where α_k is the thermal diffusivity of c-Si. Scaling this result to the three dimensions, the heat will outspread over a hemisphere of radius L_t after a t_c has elapsed. The temperature of the sample will be cooled down to $r_0^2(\text{ps laser}, 50\times) \times \pi \times L_{\text{thickness}} / (2/3 \times \pi \times L_t^3)$ of its original. For the 6.6 nm thick MoS_2 sample, $\Delta T_5 = 15.8$ K/mW. In our ps laser Raman experiment, the highest temperature of MoS_2 is heated to $\Delta T_{6.6\text{nm}} = 15.8\ \text{K/mW} \times 6.93\ \text{mW} = 109\ \text{K}$. It will be cooled down to only around 0.02 K before the next pulse arrives. As a result, we will not consider this pulse accumulation effect from substrate in this work.

S5. The effect of optical properties

Table S2. The study results for the effect of the optical properties of MoS_2 on final normalized RSC values. By varying the complex index of MoS_2, based on the calculated temperature rise ΔT_1 to ΔT_6, $\Theta(MoS_2)$ has a variance of less than one thousandth of that based on the original complex index (4.4-1.1*i*).

Objective lens	**Complex index**	ΔT_1 **(K)**	ΔT_2 **(K)**	ΔT_3 **(K)**	ΔT_4 **(K)**	ΔT_5 **(K)**	ΔT_6 **(K)**	$\Theta(MoS_2)$
20×	4.4-1.1*i*	1.95	0.168	0.124	0.162	17.24	0.629	0.097
	2.2-1.1*i*	2.30	0.203	0.146	0.197	20.30	0.762	+0.11‰
	5.5-1.1*i*	1.80	0.143	0.114	0.139	15.87	0.538	+0.05‰
	4.4-0.55*i*	2.08	0.193	0.132	0.187	18.43	0.723	-0.21‰
	4.4-2.2*i*	1.70	0.129	0.108	0.125	15.05	0.484	-0.02‰
100×	4.4-1.1*i*	11.80	0.335	0.242	0.358	17.24	0.629	0.550
	2.2-1.1*i*	13.89	0.406	0.285	0.433	20.31	0.762	+0.21‰
	5.5-1.1*i*	10.86	0.287	0.223	0.306	15.87	0.538	+0.50‰
	4.4-0.55*i*	12.61	0.385	0.259	0.411	18.43	0.723	-0.13‰
	4.4-2.2*i*	10.29	0.258	0.211	0.275	15.05	0.484	-0.10‰

S6. Sensitivity of *D* and *R* to MoS_2 in-plane thermal conductivity

To study how *D* and *R* value is sensitive to the MoS_2 in-plane thermal conductivity ($k_{||}$), we perform the 3D modeling by varying the $k_{||}$ value. Without changing other parameters, we calculate the normalized RSC values to extract *D* and *R* as shown in Table S3. While increasing $k_{||}$ by 10%, *R* is not sensitive to that. This is because *D* and $k_{||}$ only contribute to the in-plane thermal energy distribution. However, *D* is very sensitive to $k_{||}$ and decreases by 16.6%. During the diffusion process, the hot carrier only carries ~60% (E_g/E) of the photon energy and the phonon could carry the total photon energy. To keep the same temperature drop, *D* is supposed to change more.

Table S3. The study results for the sensitivity of *D* and *R* to MoS_2 in-plane thermal conductivity ($k_{||}$). By only varying $k_{||}$ of MoS_2, based on the calculated temperature rise ΔT_1 to ΔT_6, *D* is sensitive to the $k_{||}$ value.

Thermal conductivity $k_{||}$ (W/m·K)	*D* (cm^2/s)	*R* (10^{-7} K·m^2/W)
52	$0.637^{+0.193}_{-0.154}$	$1.75^{+0.08}_{-0.08}$
57.2 (+10%)	$0.531^{+0.163}_{-0.134}$ (-16.6%)	$1.75^{+0.08}_{-0.08}$
46.8 (-10%)	$0.771^{+0.206}_{-0.169}$ (+21.0%)	$1.76^{+0.08}_{-0.08}$

S7. Interference Induced Raman Enhancement

The multiple reflections of the incident laser beam and Raman signal within the supported nanosheets and the spacing have been studied in previous work.[6] The net absorption factor (F_{ab}) is given by

$$F_{ab} = t_1 \frac{(1 + r_2 r_3 e^{-2i\beta_2}) e^{-i\beta_x} + (r_2 + r_3 e^{-2i\beta_2}) e^{-i(2\beta_1 - \beta_x)}}{1 + r_2 r_3 e^{-2i\beta_2} + (r_2 + r_3 e^{-2i\beta_2}) r_1 e^{-2i\beta_1}}, \quad \text{(S10)}$$

where $t_1 = 2\tilde{n}_0/(\tilde{n}_0 + \tilde{n}_1)$, $r_1 = (\tilde{n}_0 - \tilde{n}_1)/(\tilde{n}_0 + \tilde{n}_1)$, $r_2 = (\tilde{n}_1 - \tilde{n}_2)/(\tilde{n}_1 + \tilde{n}_2)$, and $r_3 = (\tilde{n}_2 - \tilde{n}_3)/(\tilde{n}_2 + \tilde{n}_3)$ are Fresnel transmittance and reflection coefficients for the interface involving air (0), MoS_2 nanosheets (1), air (2), and Si (3). $\tilde{n}_0$, $\tilde{n}_1$, $\tilde{n}_2$ and $\tilde{n}_3$ are the refractive indices for air, MoS_2 nanosheets, air, and c-Si, respectively. $\beta_x = 2\pi x \tilde{n}_1/\lambda$, $\beta_1 = 2\pi d_1 \tilde{n}_1/\lambda$ and $\beta_2 = 2\pi d_2 \tilde{n}_2/\lambda$, where x is the depth of the point where interaction occurs, λ is the wavelength of the incident laser (532 nm), d_1 and d_2 are the thickness of MoS_2 nanosheets and c-Si, respectively. We assume there is no spacing between MoS_2 nanosheets and the c-Si substrate. The Raman intensity variation with the MoS_2 thickness will be compared with the experimental results to evaluate whether there is an interface spacing.

Similarly, the net scattering factor (F_{sc}) is described by

$$F_{sc} = t_1' \frac{(1 + r_2 r_3 e^{-2i\beta_2}) e^{-i\beta_x} + (r_2 + r_3 e^{-2i\beta_2}) e^{-i(2\beta_1 - \beta_x)}}{1 + r_2 r_3 e^{-2i\beta_2} + (r_2 + r_3 e^{-2i\beta_2}) r_1 e^{-2i\beta_1}}, \quad \text{(S11)}$$

where $t_1' = 2\tilde{n}_1/(\tilde{n}_0 + \tilde{n}_1)$ and λ is the wavelength of the E^1_{2g} mode of MoS_2. Then we could express the theoretical Raman intensity (F) of MoS_2 as

$$F = \int_0^{d_1} \left| F_{ab} F_{sc} \right|^2 dx , \tag{S12}$$

In the calculation, the refractive index of different thick MoS_2 nanosheets is extracted from Yim *et al*.'s work.[3] The refractive indices of c-Si are 4.15 + 0.05*i* and 3.99 + 0.33*i* for incident laser and Raman scattering, respectively.

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