Supporting Information to

Bandgap Modulation of MoS_2 Monolayer by Thermal Annealing and Quick Cooling

Hong-Quan Zhao*[a], Xin Mao[b], Dahua Zhou*[a], Shuanglong Feng*[a], Xuan Shi[a], Yong Ma[a], Xingzhan Wei[a], Yuliang Mao*[b]

1. Theoretical estimation of the cooling speed by sample annealing and quick cooling (quenching)

The cooling speed by thermal modulation of annealing and quick cooling on the MoS_2 monolayer is difficult to be experimentally measured in a direct way due to the small MoS_2 monolayer sizes of ～20um and the high cooling speed. However, the cooling speed can be evaluated by construction of proper physical modelling. Considering the atomic thickness (0.7nm-1nm) of MoS_2 monolayer, the problem can be attributed to the solution of surface cooling speed. The monolayer is supposed to be uniform at any point because of its atomic thickness, and also confirmed by the AFM measurements. Then, the problem is approximately simplified to be the analysis of a zero-dimensional model.

Suppose an arbitrary shape of material with the volume of V and surface area A, at an initial temperature T_0, the material is suddenly put into a fluid with the initial temperature of T_∞. According to the principle of conservation of energy, when the object is cooled, the heat dissipation from the object to environment by heat convection and conduction equals the reduction of internal energy of the object:[1]

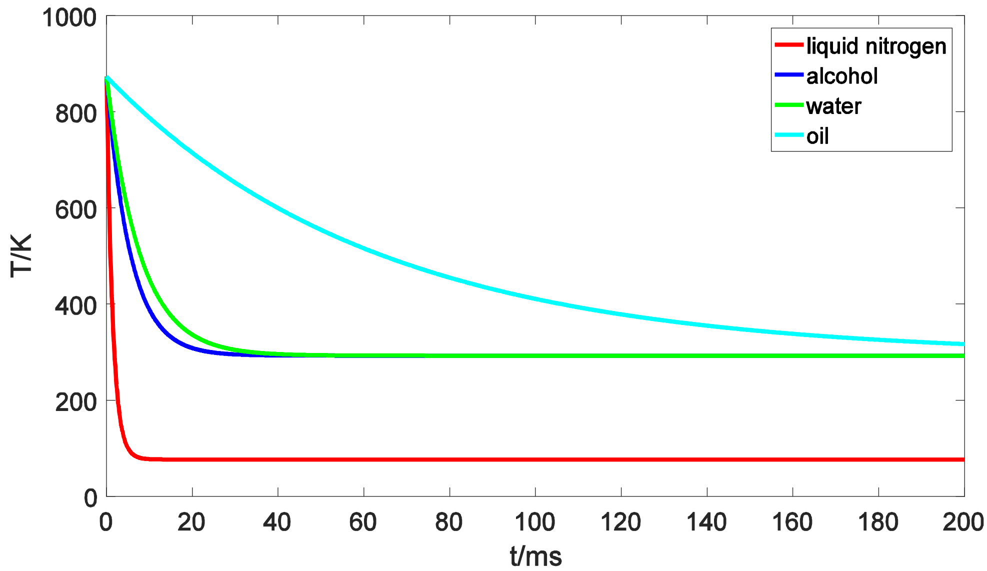
$$-\rho c V \frac{dT}{d\tau} = h\,A(T_0 - T_\infty)$$

Where ρ and c are the density and heat capacity of the object, respectively, h is the heat exchange coefficient of the cooling media, T is the temperature of the object at an arbitrary time, T_0 is the initial temperature of the object (or the annealing temperature), and T_∞ is the room temperature (20℃) since the volume of the cooling media is much more bigger than the volume of the object, and τ is the cooling speed of the object.

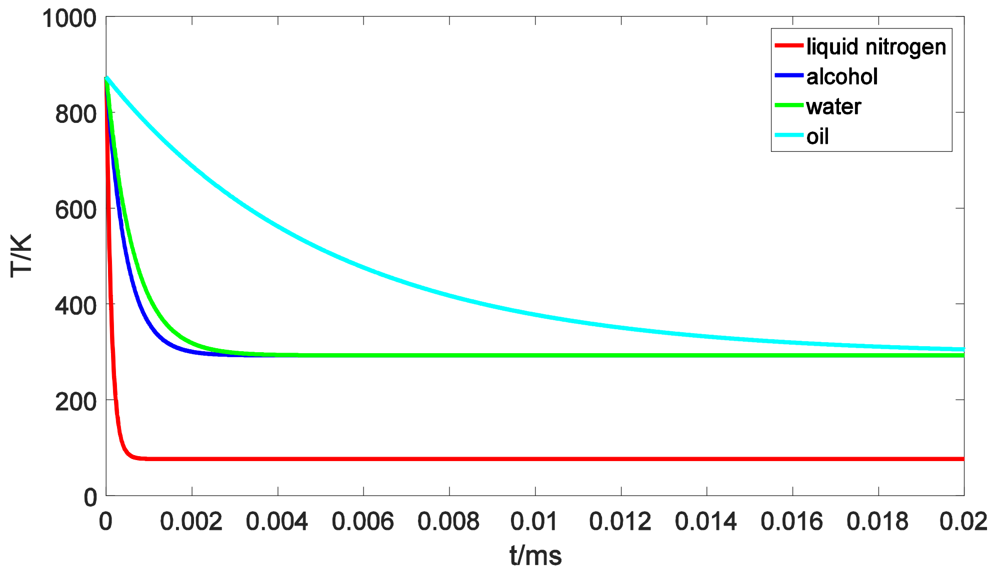
We estimated the cooling speed of MoS_2 monolayer on SiO_2/Si (300nm/300um) substrate with the silicon wafer of 5mm×5mm sizes and 0.3mm of thickness. The result is shown in Fig. S1a. It shows that the cooling speed is dependent on the cooling media. Different cooling media conditions including liquid nitrogen, alcohol, pure water, and oil are estimated in Fig. S1, and it shows that sample temperature decreased from 600℃of annealing and initial cooling temperature to the room temperature in ～10 to 15 milliseconds. Meanwhile, If consider the MoS_2 monolayer independently, the cooling speed is much more higher due to the ～20um×20um of MoS_2 size and ～1nm of thickness, and the temperature of MoS_2 monolayer decreased from

600℃ to the room temperature in ～1 to 1.5 microseconds, the result is shown in Fig. S1b.

According to the previous report, the crystalline relaxation time (T_1) of MoS_2 material is ～15 milliseconds,[2] which is a little bigger or comparable to the present estimation of cooling speed of the whole MoS_2 on SiO_2/Si wafer with 0.3mm of thickness cooled in alcohol, but much bigger than the cooling time of independent MoS_2 monolayer condition. Since the thickness of MoS_2 monolayer on SiO_2/Si surface is ～1nm, which can be approximately seen as the surface of Si, the estimated cooling speed of this monolayer is in the order from several microsecond to millisecond, smaller than the crystalline relaxation time of MoS_2 material.



(a)

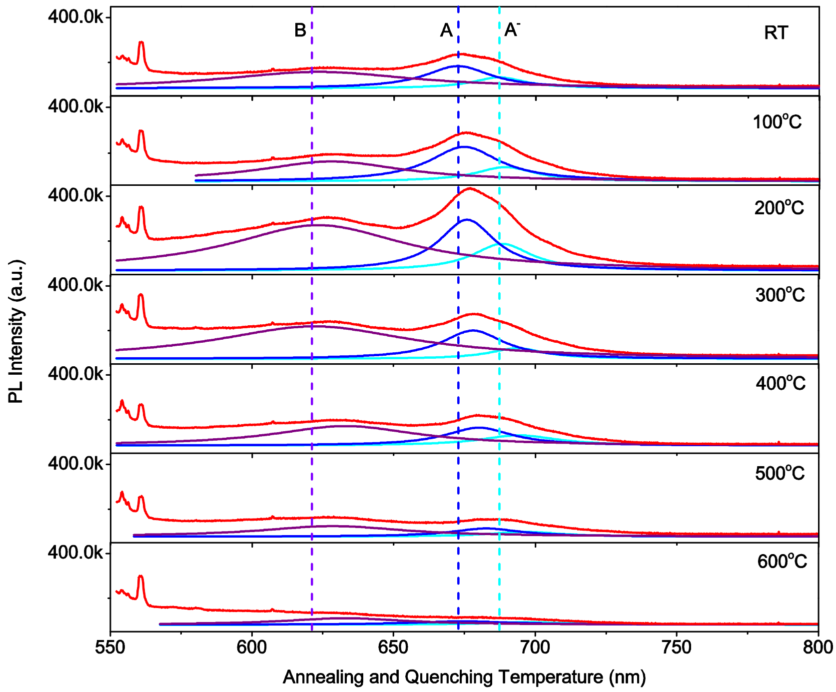


(b)

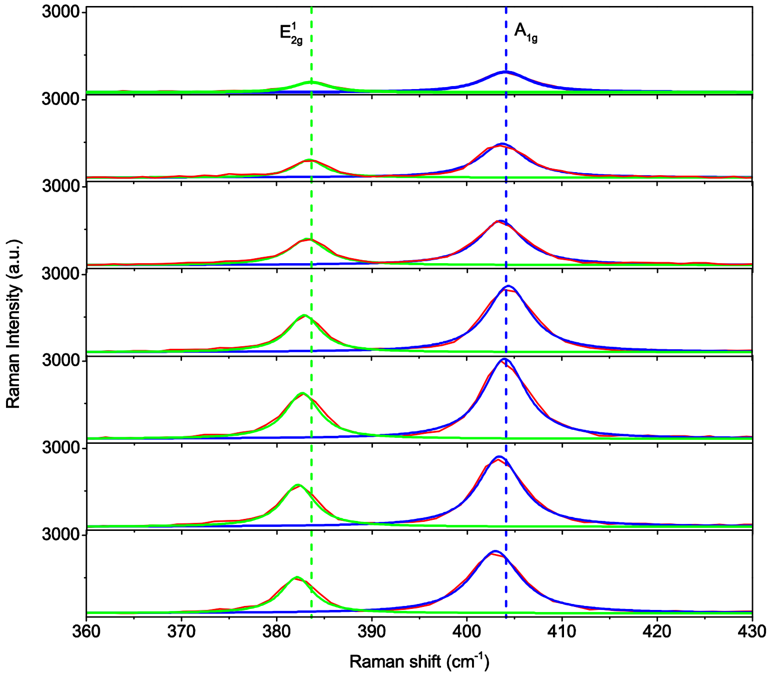
Figure S1 Cooling speed estimation of (a) MoS_2 on SiO_2/Si substrate, and (b) independent MoS_2 monolayer in cooling media of liquid nitrogen, alcohol, water, and oil, respectively. The Annealing and quick cooling initial temperature is 600℃(873K), and the final temperature is 20℃ (293K) and 77K (for liquid nitrogen).

2. Peak intensity and wavelength confirmation by Lorentzian fitting of the photoluminescence (PL) and Raman peaks.

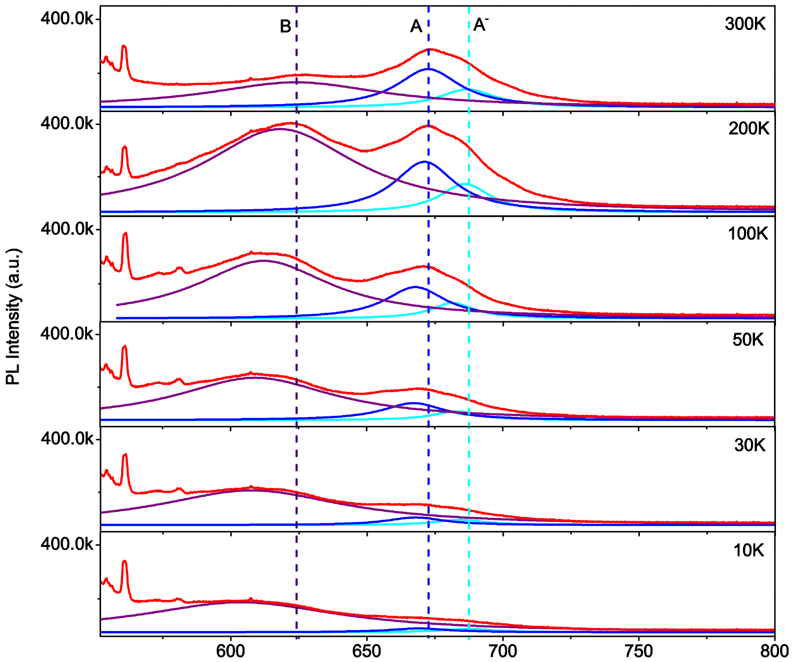
The peak intensities and wavelengths were extracted and confirmed by Lorentzian fitting of the PL and Raman peaks,[3] as we shown in Fig. S2. Figure S2a shows the Lorentzian fitted spectra of monolayer MoS_2 vacuum annealed and sudden cooled in ethanol from RT to 600℃. Line in red colour represent the extracted spectrum, and lines in cyan, blue, and purple colours represent the A^- trion, A exciton, and B exciton, respectively, which are three stable excitons in MoS_2 monolayer due to the strong spin-orbit interactions and interplay between a neutron exciton and an excessive electron.[4] Figure S2b shows the Lorentzian fitted Raman spectra of MoS_2 monolayer vacuum annealed and cooled in ethanol from RT to 600℃. Line in red colour represent the Raman spectrum, and Line in blue and green colour represent the A_{1g} and E^1_{2g} frequency modes, respectively. Figure S2c shows the Lorentzian fitted PL spectra of untreated MoS_2 monolayer measured in vacuum at temperatures from RT to 10K. Similar to figure S2a, line in red colour represent the extracted spectrum, and line in cyan, blue and purple colours represent the A^- trion, A exciton, and B exciton, respectively.



(a)



(b)



(c)

Figure S2 Lorentzian fitted (a) PL spectrum and (b) Raman spectrum of monolayer MoS_2 vacuum annealed and sudden cooled in ethanol from RT to 600℃; (c) Lorentzian fitted PL spectrum of untreated MoS_2 monolayer measured in vacuum at temperatures from RT to 10K.

3. MoS_2 monolayer annealed from RT to 600℃ at natural cooling condition

To clarify the effect of the quenching on the stress into MoS_2 monolayers, comparison of the annealed samples from RT to 600℃ with natural cooling conditions were investigated, and the results were shown in Fig. S3. Samples were prepared in the same conditions by CVD method as elaborated in the experimental section, and the seven samples were also cleaved into ～ 5mm×mm sizes from the same wafer. As the annealing temperatures increased from RT to 300℃, the A and B exciton peak intensities increased accordingly. However, as the annealing temperatures increased from 300℃ to 600℃ further, the A and B exciton peak intensities decreased quickly. The maximum peak intensity of the annealed samples was found to be appeared at 300℃. Meanwhile, about 1nm of A exciton peak wavelength drift was observed, which may due to the different annealing temperatures together with the calibration errors of the spectrometer.

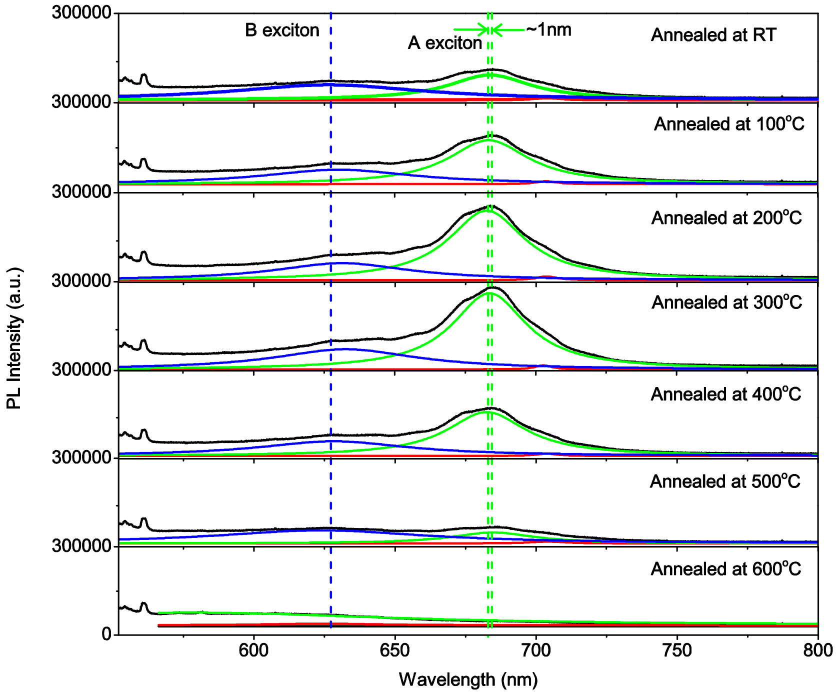


Figure S3 PL spectra of MoS_2 monolayer vacuum annealed from RT to 600℃ and cooled naturally.

References:

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