Supplementary Information

The Impact of Strain on Growth Mode in Chemical Vapor Deposited Mono- and Few-layer MoS_2

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I. ESTIMATION OF THE TOTAL AMOUNT OF GROWN MOS_2, N_{tot}

Estimation of the number of mono-layers that can form during the sulfurization with respect to the sputtered amount of Mo. This method is quite important in combination with the results from the Raman measurements, since it gives a better image on the amount of MoS_2 mono-layers that actually formed on the sample. This estimation is very important when it comes to the description of the growth process. However this estimation involves a not negligible error, estimated to be 0.5 MLE for N_{tot}. We start with the density of both materials and bring it in relation to the height of the film. The density ρ is described by:

$$\rho = \frac{m}{V} = \frac{m}{Ah} \tag{1}$$

Here A is the area of the deposited film and its height h. The mass m can be expressed as the product of molar mass M and the amount of substance n. Where the amount of substance can be expressed with the number of particles N divided by the Avogadro constant N_A.

$$m = nM = N \times \frac{M}{N_A} \tag{2}$$

Hence we get:

$$\rho = N \times \frac{M}{N_A} \times \frac{1}{Ah} \tag{3}$$

For Mo we have:

$$\rho_{Mo} = N_{Mo} \times \frac{M_{Mo}}{N_A} \times \frac{1}{Ah_{Mo}} \tag{4}$$

For MoS_2 we have:

$$\rho_{MoS_2} = N_{MoS_2} \times \frac{M_{MoS_2}}{N_A} \times \frac{1}{Ah_{MoS_2}} \tag{5}$$

A unit cell of monolayer MoS_2 contains only one Mo atom, therefore in order to form one mol of MoS_2, one mol of Mo is needed. This means their number of particles is identical $N_{MoS_2} = N_{Mo}$ giving the following relation for h_{MoS_2}:

$$h_{MoS_2} = \frac{\rho_{Mo}}{\rho_{MoS_2}} \times \frac{M_{MoS_2}}{M_{Mo}\ {}_{Mo}} \tag{6}$$

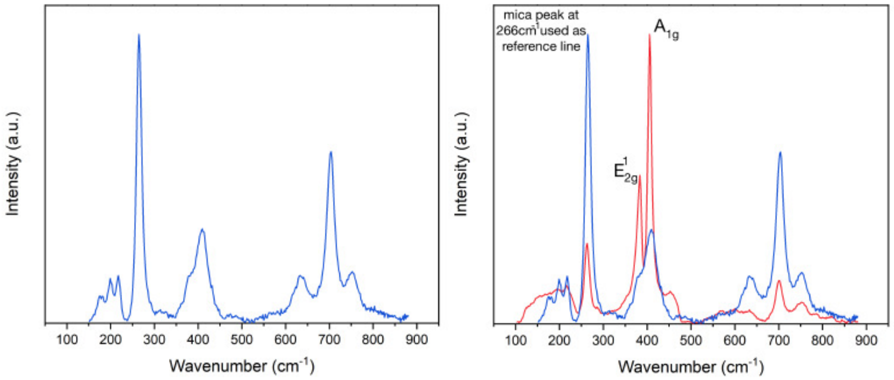
N_A cancelled out since it is a constant and the area of the deposited film is always the same for both substances so it cancels out as well. Now introducing the values ρ_{Mo} =10.22 $\frac{g}{cm^{-3}}$, ρ_{MoS_2}=5.06 $\frac{g}{cm^{-3}}$, M_{MoS_2} =160 $\frac{g}{mol}$ and M_{Mo} =96 $\frac{g}{mol}$. This gives an equation relating the height of the MoS_2 film h_{MoS_2} to the height of the Mo film h_{Mo}:

$$h_{MoS_2} = 3.4 \times_{Mo} \tag{7}$$

With the information that the sputtering machine has at 240 W a sputtering rate of 0.18 $\frac{nm}{s}$ of Mo and by assuming the sputtering time and the sputtering power correlate linearly to the thickness of deposited Mo film one can now estimate the height of MoS_2 that can be formed from a certain amount of sputtered Mo. For a sputtering power of 240 W and a sputtering time of 1 second one gets for the MoS_2 film a thickness of 0.65 nm, which corresponds to the height of a mono-layer of MoS_2.

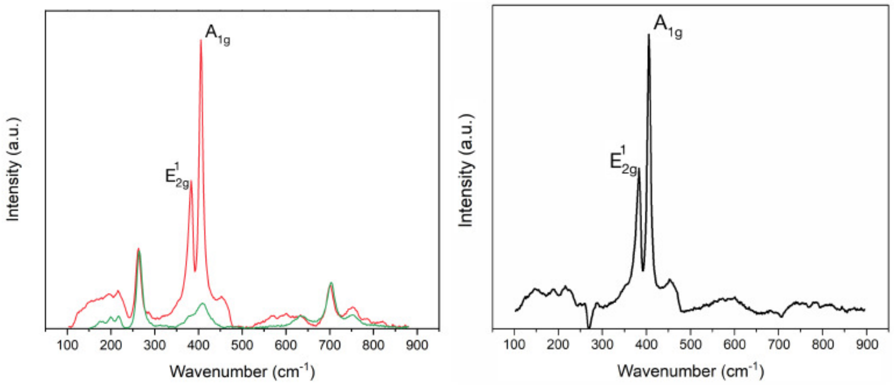
II. REMOVING MICA RAMAN SPECTRUM

Depending on the employed laser wavelength Raman spectroscopy exhibits a penetration depth of several μm, meaning that we measure not only the signal from the surface on which the laser beam is focused on, but also the underlying substrate. For the 442 nm wavelength used in this study the penetration depth is several tens of nanometers. Since the thickness of deposited material ranges in this work from roughly 0.65 nm (for one mono-layer of MoS_2) to roughly 6.5 nm (for the 10 MLE samples), it is clear that we will surely measure the Raman spectrum of the underlying mica substrate, which is attenuated with thicker films. Its Raman spectrum can be seen in (Fig. 1 a). The Raman peaks from the underlying mica substrate in the Raman spectrum of the CVD-grown MoS_2 on mica gets clear in (Fig. 1 b), where we have an overlay of both spectra, in blue for pure mica and in red for MoS_2 on mica. The first thing that points out is that in the same range of the high frequency phonon modes E^1_{2g} and A_{1g}, which are used to identify the number of MoS_2 layers, is a wide peak ranging from roughly 350 cm^{-1} to 450 cm^{-1}. This peak is problematic since its maximum value is very close to the position of the A_{1g} mode and it has a saddle point roughly at the position of the E^1_{2g} mode. Further Raman peaks from the underlying mica are the peak at 266 cm^{-1} and three peaks in the range from 600 cm^{-1} to 800 cm^{-1}. In order to properly fit the high frequency modes of MoS_2 we removed the mica signal in this region. Therefore we used the mica peak with the highest intensity at $266\,cm^{-1}$ as a reference peak. This peak is then scaled to the same intensity as the $266\,cm^{-1}$ mica peak that can be also identified in the MoS_2 spectrum (Fig. 1 c). After subtracting the pure mica signal it is possible to remove the mica influence especially in the region of interest from $350\,cm^{-1}$ to $450\,cm^{-1}$ (Fig. 1 d). These peaks could then be properly fitted and the influence of the mica substrate could be removed.



(a) Raman spectra of mica

(b) Raman spectrum of MoS_2 CVD-grown on mica (red) overlayed with the sepctrum of pure mica (blue)



(c) Raman spectrum of mica (green) fitted to the spektrum of MoS_2 on mica (red)

(d) Deconvoluted Raman-active high frequency modes of MoS_2

FIG. 1. Treatment of the Raman spectrum of CVD-grown MoS_2 on mica: Therefore the Raman spectrum of pure mica (a), its influence gets clear when overlayed with the spectrum of CVD-grown MoS_2 on mica (b), has to be fitted to the Raman spectrum of CVD-grown MoS_2 on mica (c). The reference peak is the mica peak at $266\,cm^{-1}$. Afterwards the mica signal can be subtracted and the results are the properly deconvoluted high frequency phonon modes E^1_{2g} and A_{1g} (d).

III. RAMAN SPECTRA OF MOS_2

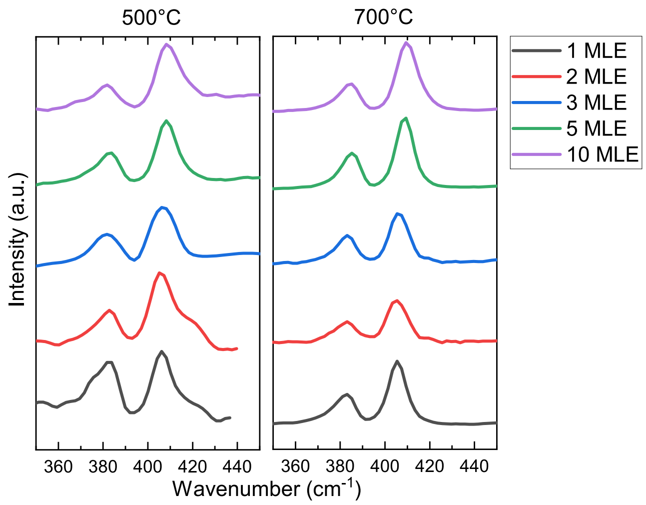
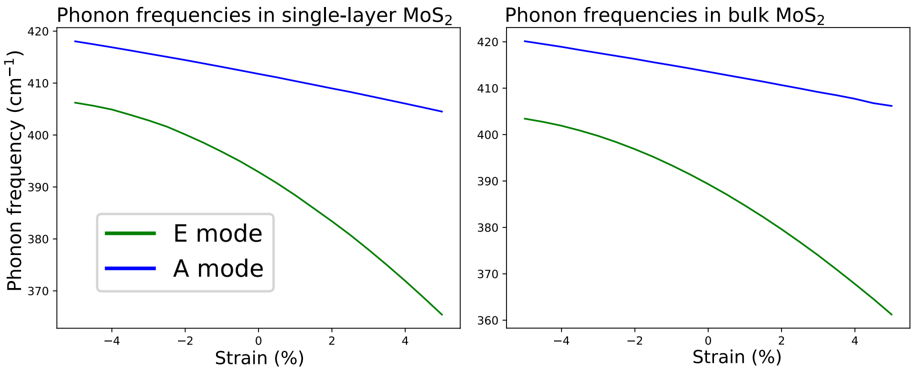


FIG. 2. Raman spectra of the sample set sulfurized at 500°C (on the left) and at 700°C (on the right). From these spectra the Raman spectrum from mica is already removed.

In the Raman spectra of the 1 MLE and 2 MLE samples sulfurized at 500°C broader peaks for the high frequency phonon modes E^1_{2g} and A_{1g} are present. However, these are not real since they are related to the removal of the Muscovite mica Raman spectrum.

IV. PHONON FREQUENCIES FROM DFT CALCULATIONS


Phonon frequencies in single-layer MoS_2

Phonon frequencies in bulk MoS_2

FIG. 3. Phonon frequencies for mono-layer (on the left) and bulk (on the right) MoS_2 from DFT calculations in the LDA.

V. GOLD ON MUSCOVITE MICA

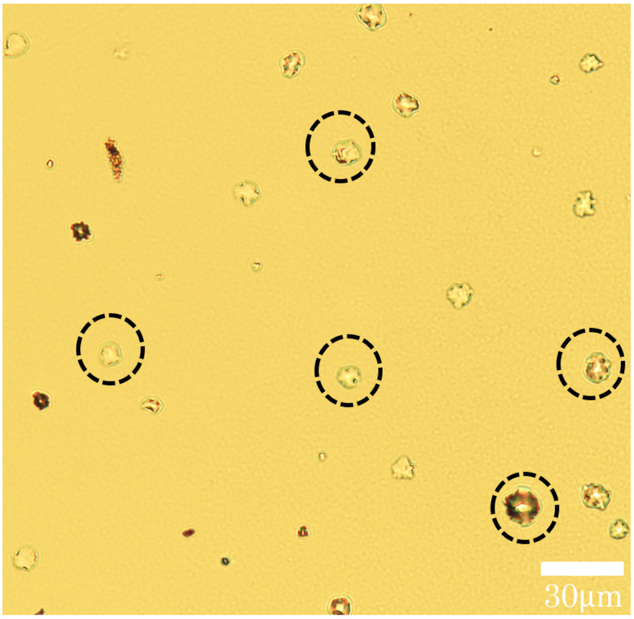


FIG. 4. Muscovite mica with 200 nm of gold, forms bulges after annealing.

On the Muscovite mica substrate we deposited 200 nm of gold. Then the gold covered mica substrate was flame annealed at roughly 700°C leading to the formation of bulges due to the expansion of encapsulated gas between the mica sheets.

VI. ALL AFM TOPOGRAPHIES

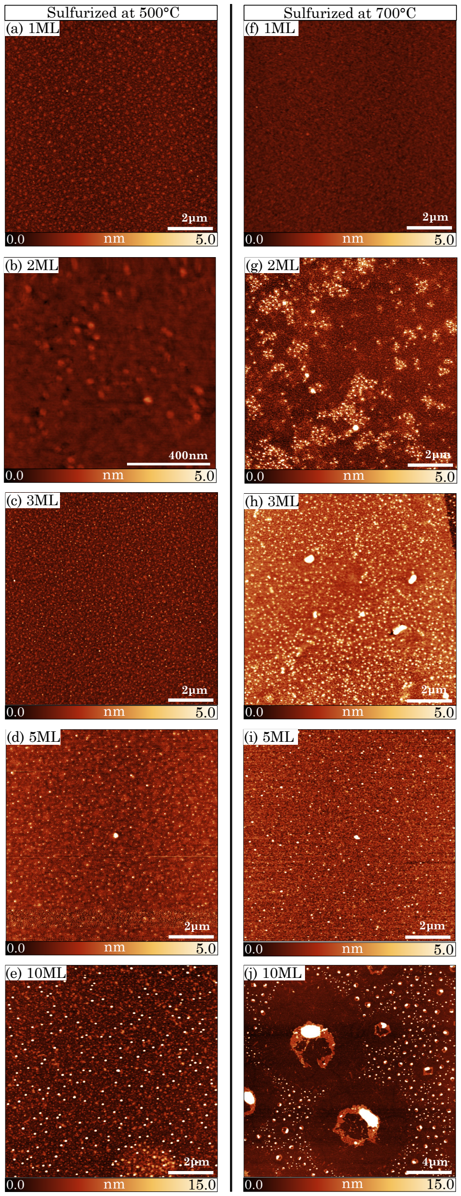


FIG. 5. AFM topography images for different thicknesses of MoS_2 films grown on mica for two different sulfurization temperatures, (a)-(e) for the 500°C and (f)-(j) for the 700°C sulfurization. Height scale is adjusted for maximum contrast and depicted below each image. A different growth mode is observed for the two sulfurization temperatures.

The 10 ML 700°C image shows a 10x10 μm^2 topography to better represent the enhanced island growth. On this sample the MoS_2 forms large structures of up to 120 nm in height sitting on a ring with 5-10 nm in height, while there are also smaller structures with the same shape, which are dominating the surface coverage. For the 5 ML 700°C sample the amount of island structures is reduced compared to the 3 ML 700°C sample. This is not an indication of reduced island growth since the island structures for the 5 ML 700°C sample are much larger in height

VII. PHOTOLUMINESCENCE (PL)

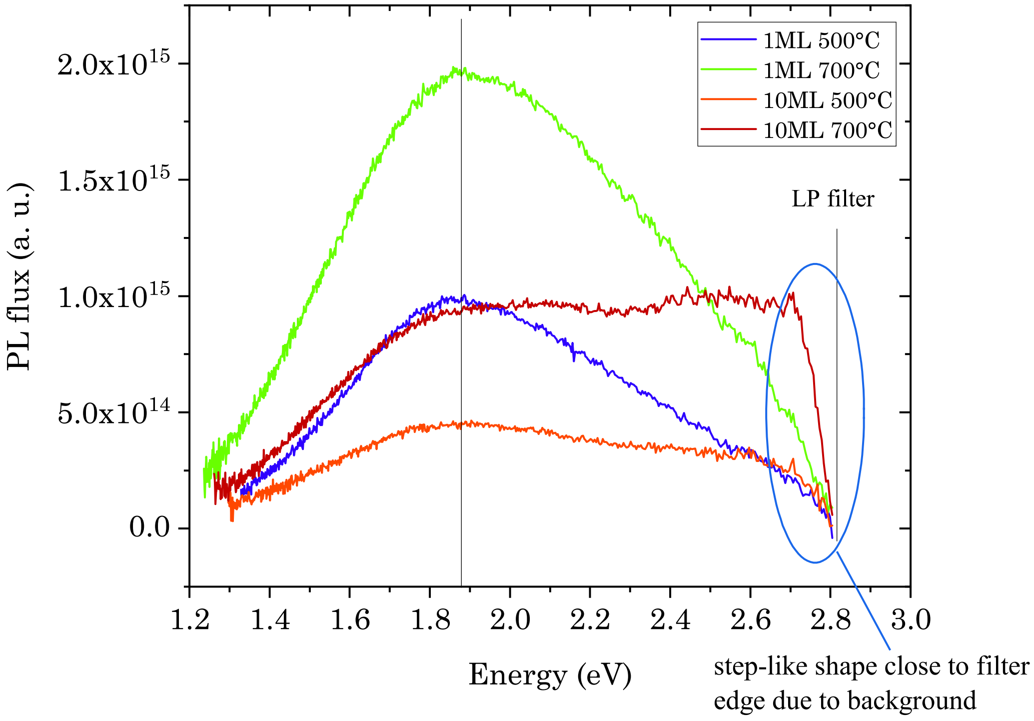


FIG. 6. PL from the 500°C 1 ML, 10 ML and 700°C 1 ML, 10 ML samples. From there one could conclude that the 1 ML samples indeed showed a direct band gap transition at 1.88 eV, characteristic for mono-layer MoS_2, while the 1 ML samples remain flatter in this region. We are not confident that this luminescence actually originates from the MoS_2 since the width of the peak is too broad. This is corroborated by the measurements on the 10 ML films where we do see a reduction of this peak but the shape is still visible. Therefore we conclude that the PL we observe is not originating from the MoS_2 but rather from the mica films. We emphasize that these measurements were the only ones where we could see a defined peak at the expected position of the MoS_2.

VIII. INFLUENCE OF 500°C SULFURIZATION ON A BARE MUSCOVITE MICA SUBSTRATE

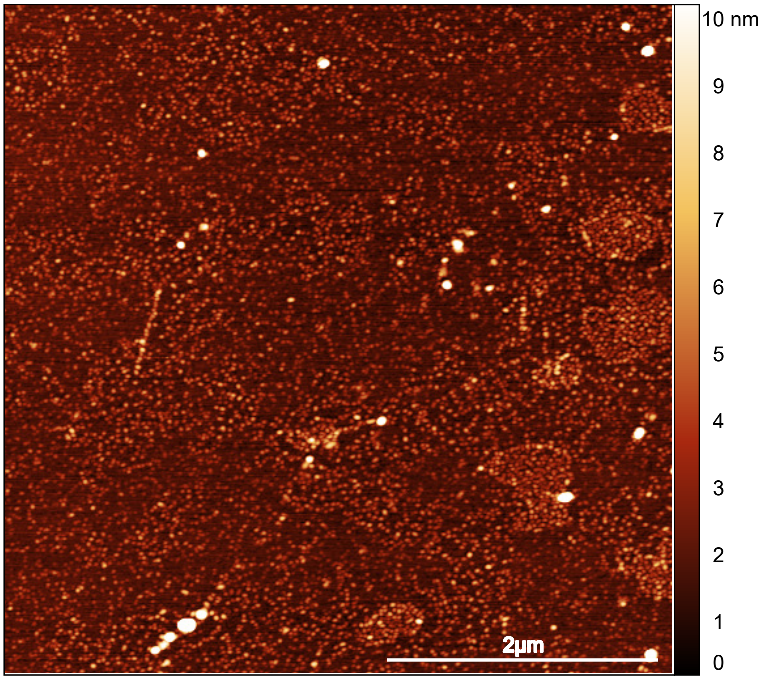


FIG. 7. Bare Muscovite mica substrate being sulfurized at 500°C. A severe roughening can be observed. This kind of roughening is not visible on the MoS_2 covered samples indicating that the metallic Mo layer protects the mica during sulfurization.

IX. FWHM OF THE RAMAN PEAKS OF THE HIGH FREQUENCY PHONON MODES

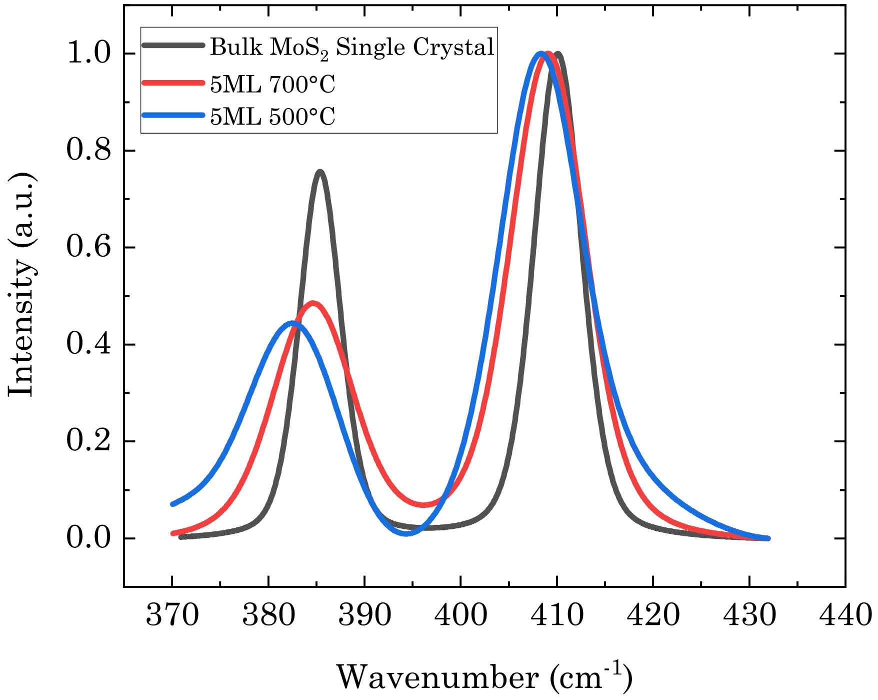


FIG. 8. Comparing the FWHM of the Raman peaks of the high frequency phonon modes A_{1g} and E^1_{2g} of a bulk single crystal of MoS_2 with those from the CVD grown 5ML 500°C and 5ML 700°C samples. It is clear that the latter two show broader peaks. Three different effects cause this. Firstly, the removal of the Muscovite mica Raman spectrum (see SI Figure 1), causes especially for the thinner MoS_2 films a broadening of the Raman peaks. Secondly, the low crystallinity (small grains) of the CVD grown samples compared to the bulk single crystal lead to further broadening. Lastly, we were limited in using the 442 nm laser line for the Raman spectroscopy, which had a worse resolution compared to the 532 nm and 622 nm wavelengths. The reason why the 442 nm wavelength was used was that the other two that were available in our system caused an even stronger luminescence background from the mica substrate.

X. RAMAN MAPPING

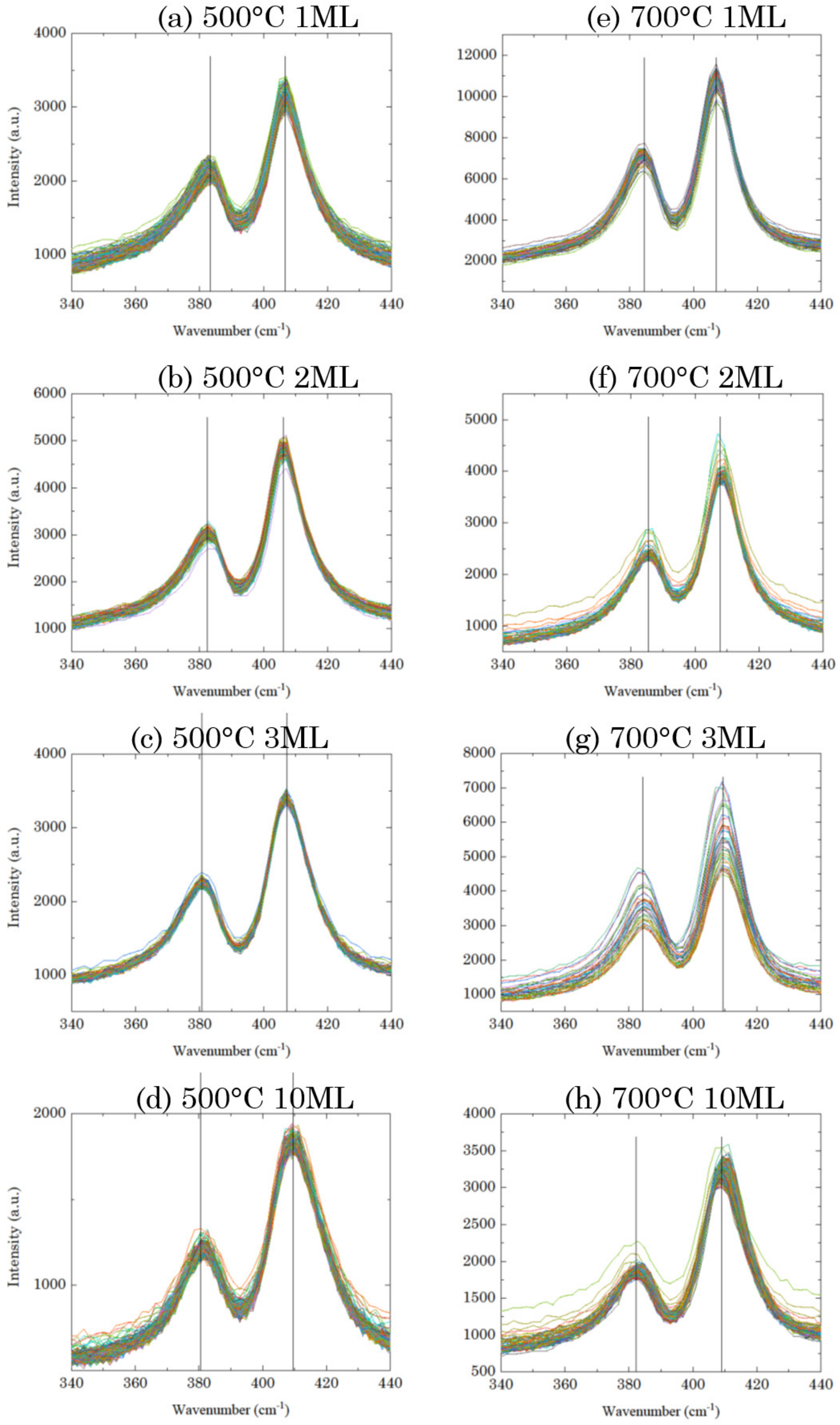


FIG. 9. Raman peaks of the high frequency phonon modes A_{1g} and E^1_{2g} for the 500°C set (a)-(d) and for the 700°C set (e)-(h). On each sample around 100 spectra were measured on different spots to check for uniformity.

The Raman spectra on each sample show overall a uniform coverage with MoS_2. This uniformity in the Raman spectra is of course limited to the lateral resolution of the Raman spectroscope. This resolution is limited by the laser spot size of roughly 1μm in diameter. Hence, when scanning MoS_2 films where the island structures are evenly distributed on the surface and their spacing to neighboring islands is less than 1μm, the Raman spectrum is averaging the signal coming from the fully covering layers and the island structures. The small island structures are not individually resolved with the Raman spectroscope. Therefore, the uniformity of the Raman spectra does not contradict the non-uniformity of the AFM topographies.