Sulphur concentration influence on morphology and optical properties of MoS_2 monolayers

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ABSTRACT

In this work we present the sulphur concentration influence on the morphology and optical response of MoS_2 monolayers. The CVD grown samples from liquid-based Mo-precursors were synthesized under different growth conditions and their optical properties were investigated upon synthesis. Samples with Mo:S ratio close to 1:2 have symmetrical triangular shape with even edges and their optical response was good or excellent. The best optical response was obtained at high growth temperatures (875-900°C), medium argon flow (75 sccm) and medium sulphur temperature (140°C). AFM and SEM measurements confirmed high-quality crystalline growth with no evidence of grain boundaries.

MATERIALS AND METHODS

MoS_2 samples were made using liquid Mo-precursor and sulphur powder. Liquid Mo-precursor contained mixture of DI water-based solution (15.4 ppm) of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}$ (**AHM**) and DI water-based solution (15.4 ppm) of sodium molybdate Na_2MoO_4 (**NaMo**) mixed in equal parts. For synthesis we used chemical vapour deposition (CVD) setup pictured below.

Optical characterization was done using confocal microscope in backscattered configuration which serves for absorption, photoluminescence (PL) and Raman spectra measurements, as well as for optical mapping of samples. Excitation laser energy was 2.33 eV (532 nm) and laser power on sample was 500 μW.

Complementary structural characterizations by atomic force microscope (AFM) and scanning electron microscope (SEM) were used to determine existence of grain boundaries and cracks in crystal basal plane.

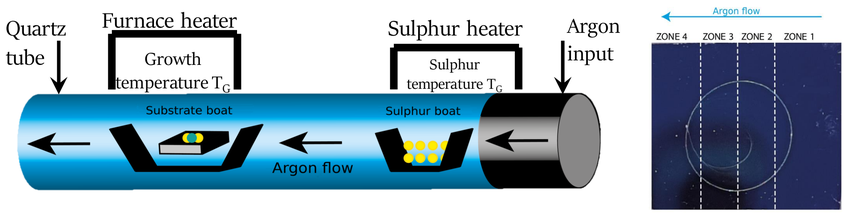

Figure 1. Left: Schematic illustration of CVD furnace. Right: Illustration of 4 zones on the substrate with respect to argon flow. Taken from [1].

The substrate was divided into 4 zones, as shown on the right part in Figure 1. From each zone we investigated one randomly chosen MoS_2 island. In this way we were able to correlate quality of MoS_2 islands with respect to the direction of argon flow.

CONCLUSION

The most powerful feature of the CVD growth technique is its high scalability. In order to develop reliable and reproducible deposition technique, control of the vapour phase precursors flow under inert atmosphere and controlled evaporation of liquid precursors are prerequisite. Samples made under the same conditions not only had the identical morphology, but the identical optical response as well. Our goal was to find optimal synthesis parameters which yield excellent optical response of MoS_2 monolayers both locally and globally, since such property is a result of high-quality electronic structure [2].

We have shown how different synthesis parameters combinations result in various MoS_2 islands, in terms of morphology and their optical response. Optical response of 1L MoS_2 islands highly depends on the sulphur concentration, which can be coarsely tuned with the change of sulphur temperature and finely tuned with change of argon flow. Samples with high sulphur concentration have visible grain-boundaries and bad optical response. On the other hand, if the stoichiometric ratio is just right, single-crystalline growth is obtained. Such samples have no visible grain-boundaries; their optical response is excellent and uniform throughout the central part of the island.

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RESULTS AND DISCUSSION

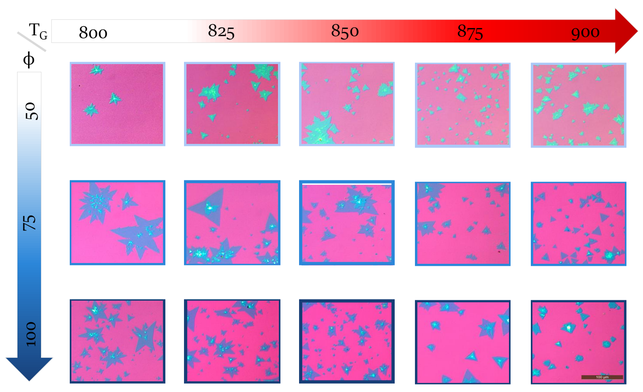

Figure 2. MoS_2 morphology dependence on the growth temperature T_G and argon flow ϕ. Sulphur temperature was set to 140°C. Scale bar is 100 μm.

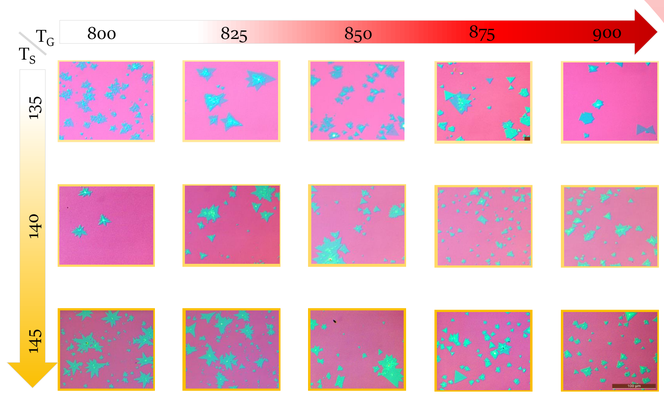

Figure 3. MoS_2 morphology dependence on the growth temperature T_G and sulphur temperature T_S. Argon flow was set to 50 sccm. Scale bar is 100 μm.

MoS_2 morphology dependence on synthesis parameters (growth temperature T_G, sulphur temperature T_S and argon flow ϕ) is shown in Figures 2. and 3. At medium argon flow lateral growth of MoS_2 islands is increased. Further increase of ϕ leads to increase of activated nucleation sites, while the lateral growth is repressed. Multilayer growth is obtained mostly at high growth temperatures. But, if the sulphur temperature is low, then multilayer MoS_2 islands are obtained throughout the growth temperature range, as demonstrated in [3].

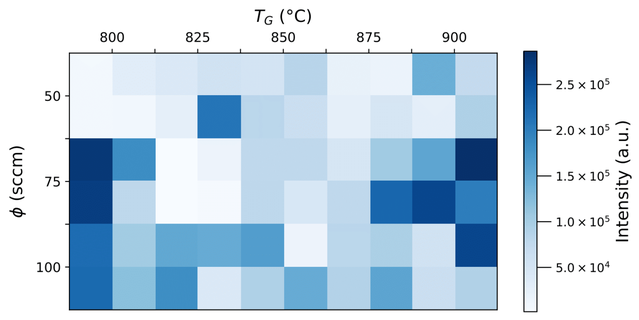

Figure 4. A exciton intensity dependence on growth temperature T_G and argon flow ϕ. Sulphur temperature is set to 140°C.

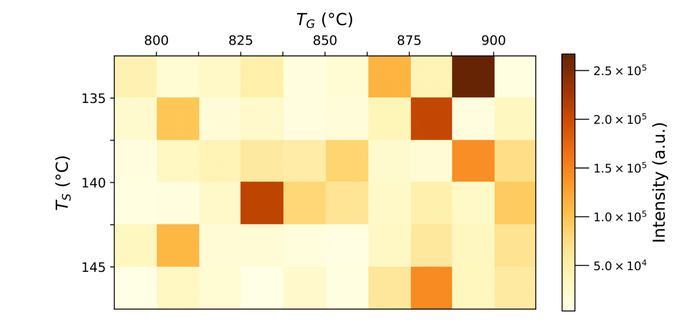

Figure 5. A exciton intensity dependence on growth temperature T_G and sulphur temperature T_S. Argon flow is 50 sccm.

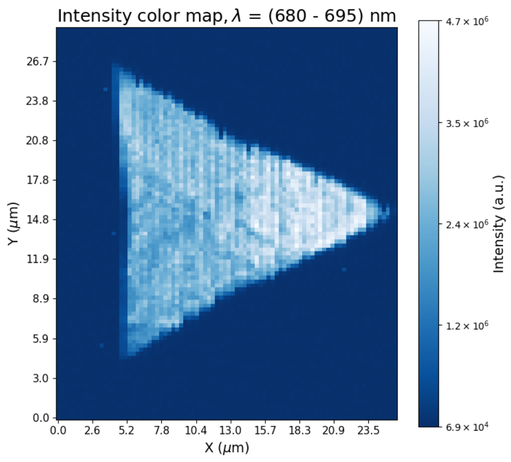

Figure 6. False-color A exciton intensity color map for sample with synthesis parameters: T_G = 825°C, T_S = 140°C, ϕ = 75 sccm.

In order to find optimal synthesis parameters for the best optical response, we compared the intensity of the A exciton peak in every sample we made. Results are shown in Figures 4. and 5. For every set of parameters there are 4 squares which represent 4 growth zones on the substrate. We concluded that for the synthesis parameters: T_G = 900°C, T_S = 140°C and ϕ= 75 sccm, the sample is homogeneous throughout the substrate, while some other combinations of low growth temperature and medium or high argon flow also yield high-quality samples. Change in sulphur temperature greatly influences the optical response of the MoS_2 islands and good optical response was realized in samples with higher growth temperatures and low to medium sulphur temperatures.

A exciton intensity map (Figure 6.) shows that samples with optimal synthesis parameters combination are homogeneous in the central part of the triangle, while the edges and vertices have lower intensity. These edge effects will be further investigated with complementary techniques and optical measurements at low temperatures.

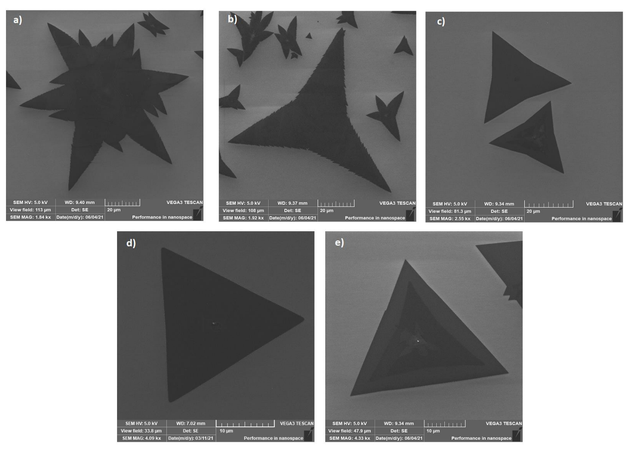

Figure 7. SEM images of MoS_2 samples grown under different conditions.

On the left: SEM images of different MoS_2 island morphologies. **(a)-(c)**: If the sulphur concentration is high, dendritic and star-shaped islands with uneven edges were obtained**; (d)** Samples with ideal stoichiometric ratio (Mo:S = 1:2) have equilateral triangular shape with even edges**; (e)** If the growth temperature is high enough (850-900°C), it increases the probability for bilayer and multilayer growth, where the top layer grows by epitaxial growth on top of the bottom layer, by activating the same nucleation centers [4].

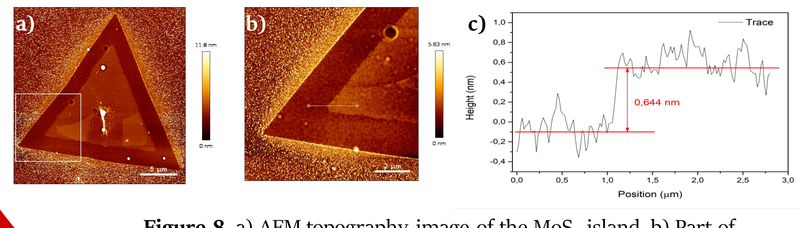

Figure 8. a) AFM topography image of the MoS_2 island. b) Part of topography map of the sample indicated with white square shown in a). White line shows the position of a line profile presented in c).

AFM measurements (Figure 8.) showed that the Si/SiO_2 substrate is densely covered with unreacted Mo-precursor due to its initial liquid phase [5]. Also, due to the presence of NaOH in the Mo-precursor mixture, the SiO_2 surface layer is etched and MoS_2 islands grow over holes visible in the images [5]. Even though the RMS roughness of the substrate is in the nm range, the MoS_2 samples have sub-nm (~ 0.2 pm) RMS roughness. Line profile on the left shows the height difference of a 2L and 1L MoS_2 which is in great agreement with the theoretical value of 0.7 nm [6].