

## Thermodynamic modeling for controlled CVD growth of MoS<sub>2</sub> atomic layers

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**Abstract:** Stimulated by the discovery of two-dimensional graphene monolayers, the inorganic graphene analogue MoS<sub>2</sub> have created great interest in the recent years. For growth of MoS<sub>2</sub> with controlled numbers of layers by CVD, vapour phase supersaturation needs to be quantitatively controlled. This can be achieved by wide variation of total reactor pressure P, growth temperature T, and flow of various gases. As CVD is a chemical process involving many solid and gaseous phases, MoS<sub>2</sub> deposition leads to films with a range of non-stoichiometry and contamination in the form of carbon, carbide(s), sulfur and metal-oxides, in various amounts. Uncontrolled compositional disturbances are extremely undesirable for electronic devices as they result in uncontrolled background. Therefore, as a prelude to the experiments, equilibrium concentrations of various condensed and gaseous phases were thermodynamically calculated as functions of CVD parameters, with Mo(CO)<sub>6</sub> and H<sub>2</sub>S as the precursors. The process uses criterion of minimization of total Gibbs free energy of the system, assuming that equilibrium prevails in the process, which is applicable when the rate of deposition is low [1].

The composition range studied was Mo(CO)<sub>6</sub>:H<sub>2</sub>S:H<sub>2</sub>=10:1:100 to 1:10:100, with T and P in the range of 100-1100°C and 20-600 Torr. The calculations indicate that pure MoS<sub>2</sub> is formed for H<sub>2</sub>S:Mo(CO)<sub>6</sub>>3.5. A typical CVD phase stability diagram at P=600 Torr, obtained from such calculations, is presented in Fig. 1(a). A ratio of Mo(CO)<sub>6</sub>:H<sub>2</sub>S=1:10, provides an optimum margin and was therefore considered for experimental deposition throughout the study. The experiments performed agree with the theoretical predications of C-free MoS<sub>2</sub>.

To obtain monolayered or few-layered MoS<sub>2</sub> films predictably with precision, kinetic control is called for and may be exercised by lowering the gas phase supersaturation. This can be achieved by increasing P and/or increasing the partial pressure of H<sub>2</sub> and CO in the system. The effect of reduction in ΔG by increasing P from 20 to 550 Torr, for experimental deposition with Mo(CO)<sub>6</sub>:H<sub>2</sub>S:H<sub>2</sub>=1:10:100 in the thermodynamically permissible window at 850°C is shown in Fig. 1(b) to indicate bulk to monolayer transition as P increases. The CVD phase stability diagram as a function of H<sub>2</sub>-flow predict co-deposition of Mo<sub>2</sub>C at higher T and higher H<sub>2</sub> flow, but pure MoS<sub>2</sub> is thermodynamically permissible till 956°C at highest H<sub>2</sub> flow. Higher P (= 850 Torr) and higher H<sub>2</sub> flow, in the thermodynamically permissible window, was observed to improve the MoS<sub>2</sub> monolayer domain size, as shown in the SEM micrographs in Fig. 1(c). Introduction of CO in the system also helped in improving the microstructure by further reduction of ΔG.

### References:

[1] S. Dhar, A. Varade and S. A. Shivashankar, *Bull. Mater. Sci.*, **34** (2011) 11.

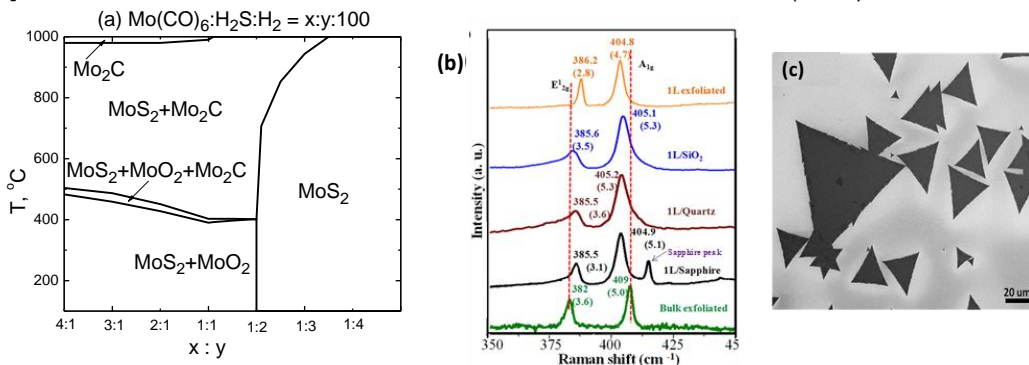


Figure 1(a). CVD phase stability diagrams with varying H<sub>2</sub>S:Mo(CO)<sub>6</sub>, (b) Raman spectra indicating bulk to monolayer transition as P increases from 20 to 550 Torr at 850°C, and (c) SEM micrograph showing the triangular islands at 850 Torr and 1000 H<sub>2</sub>.