Title: Controlling the Epitaxial Orientation of Wafer-Scale MoS_2 Monolayers on C-plane Sapphire

Authors: Chen Chen, Rohini Sanikop, Andrew R. Graves, and Joan M Redwing

Abstract (400 words/2500 characters)

Monolayer molybdenum disulfide (MoS_2) is a two-dimensional direct band gap semiconductor with promising electrical properties that are of interest for next-generation nanoelectronics. Epitaxial growth of MoS_2 monolayers on c-plane sapphire substrates has emerged as a key synthesis method for single-crystal wafer-scale films. However, the in-plane epitaxial alignment of MoS_2 relative to the underlying sapphire has been observed to vary depending on the specific growth technique employed. Epitaxial MoS_2 films grown by metalorganic chemical vapor deposition (MOCVD) using $Mo(CO)_6$ and H_2S in a H_2 carrier gas exhibit direct in-plane alignment such that $(11\bar{2}0)$ MoS_2 ∥ $(11\bar{2}0)$ α-Al_2O_3.[1] In contrast, MoS_2 films grown using MoO_3 and sulfur powder in an Ar carrier gas exhibit a 30° rotation such that $(10\bar{1}0)$ MoS_2 ∥ $(11\bar{2}0)$ α-Al_2O_3.[2] In both cases, 60° rotated twin domains are also present due to the non-centrosymmetric lattice of MoS_2. While the specific epitaxial alignment is associated with the atomic arrangement and chemistry of the sapphire surface, its dependence on growth chemistry is not well understood.

Recently, we have investigated the epitaxial growth of MoS_2 on sapphire using MoO_2Cl_2 as the molybdenum precursor in an MOCVD process instead of the more commonly used $Mo(CO)_6$ source. The MoS_2 monolayers were grown at 1000 °C using MoO_2Cl_2 and H_2S with nitrogen as the carrier gas. The nucleation density of MoS_2 on sapphire was found to be significantly reduced using MoO_2Cl_2 compared to $Mo(CO)_6$ resulting in larger domain sizes prior to coalescence and an overall improvement in crystal quality as assessed by in-plane XRD diffraction. Interestingly, the in-plane epitaxial orientation of the MoS_2 domains was found to vary depending on the S/Mo ratio employed during growth. Lower S/Mo ratios resulted in direct in-plane alignment $(11\bar{2}0)$ MoS_2 ∥ $(11\bar{2}0)$ α-Al_2O_3 with R0°/R60° rotational twin domains while the epitaxial orientation was observed to shift to $(10\bar{1}0)$ MoS_2 ∥ $(11\bar{2}0)$ α-Al_2O_3 with R±30° rotational twins at higher S/Mo ratios.

By controlling the miscut direction of the sapphire substrate, it was possible to break the degeneracy of the two antiparallel MoS_2 twin domains and promote unidirectional single-domain alignment. The use of c-plane sapphire substrates with 0.2° miscut toward the M-axis resulted in unidirectional domains for MoS_2 grown at lower S/Mo ratios while substrates

with 1.0° miscut toward the a-axis promoted unidirectional domains for MoS_2 grown at higher S/Mo ratios. The results demonstrate the need to carefully control both the growth chemistry and sapphire substrate miscut to yield high-quality MoS_2 epitaxial monolayers.

Reference:

(1) Chen, C.; Trainor, N.; Kumari, S.; Myja, H.; Kümmell, T.; Zhang, Z.; Zhang, Y.; Bisht, A.; Sadaf, M. U. K.; Sakib, N. U.; Han, Y.; Mc Knight, T. V.; Graves, A. R.; Leger, M. E.; Redwing, N. D.; Kim, M.; Kowalczyk, D. A.; Bacher, G.; Alem, N.; Yang, Y.; Das, S.; Redwing, J. M. Effect of Growth Temperature on the Microstructure and Properties of Epitaxial MoS2 Monolayers Grown by Metalorganic Chemical Vapor Deposition. *Journal of Vacuum Science & Technology A* **2024**, *42* (2), 22201. https://doi.org/10.1116/6.0003296/3261677.

(2) Li, T.; Guo, W.; Ma, L.; Li, W.; Yu, Z.; Han, Z.; Gao, S.; Liu, L.; Fan, D.; Wang, Z.; Yang, Y.; Lin, W.; Luo, Z.; Chen, X.; Dai, N.; Tu, X.; Pan, D.; Yao, Y.; Wang, P.; Nie, Y.; Wang, J.; Shi, Y.; Wang, X. Epitaxial Growth of Wafer-Scale Molybdenum Disulfide Semiconductor Single Crystals on Sapphire. *Nature Nanotechnology 2021 16:11* **2021**, *16* (11), 1201–1207. https://doi.org/10.1038/s41565-021-00963-8.