Impact of sapphire surface preparation on the MOCVD of epitaxial MoS_2 thin films

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In view of potential commercialization and mass production of electronic-grade transition metal dichalcogenides (TMDs) for next-generation semiconductor applications, metal-organic vapor deposition (MOCVD) is a promising fabrication method to meet the demand of wafer-scale homogenous TMD thin films. [1] In this context, sapphire (a-Al_2O_3) is an industrially important and widely available substrate enabling TMD epitaxy due to its crystallographic compatibility, and its stability in harsh growth conditions. Recent studies have highlighted controlled Al_2O_3 surface step topography to be key for edge-guided, unidirectional domain nucleation as a route towards single-crystalline TMDs, e.g. by using Al_2O_3 wafers with custom-manufactured miscut, [2] or by process control during MOCVD. [1] Moreover, Al_2O_3 surface reconstruction with Al-rich termination has been found to impact heteroepitaxial TMD registry. [3] However, optimal sapphire engineering for TMD epitaxy remains elusive due to case-specific, and complex interplay between surface and synthesis conditions, and the applied precursor chemistry. [4]

In this work, we investigate the MOCVD of epitaxial MoS_2 thin films grown from $Mo(CO)_6$ and dimethyl sulfide $(CH_3)_2S$ on distinct Al_2O_3 surfaces, employing in-depth characterization via atomic force microscopy (AFM), reflection high-energy electron diffraction (RHEED), grazing incidence X-ray diffraction (GIXRD), and Raman and X-ray photoelectron spectroscopy (XPS). We compare Al_2O_3(0001) substrates with standard ±0.2° and unconventionally low ±0.05° miscut angles after thermal annealing (1050-1200°C), resulting in atomically-smooth, stepped surfaces with defined step shape and terrace width. Additionally, we control sapphire termination in O_2- and H_2-annealing atmosphere, and obtain (1×1) and Al-rich $\left(\sqrt{31} \times \sqrt{31}\right)R9°$ reconstruction, respectively. While MOCVD on O_2-annealed sapphire yields uniform, triangular MoS_2 domains, MOCVD on H_2-annealed, ragged-stepped surface shows disturbed domains and increased carbon incorporation, as detected by Raman and XPS analyses, possibly induced by the Al-rich sapphire surface chemistry. This is further supported by AFM images showing non-uniform, mosaic terrace phase contrast on H_2-annealed sapphire, suggesting surface-selective MoS_2 domain nucleation, which sheds light on the importance of sapphire surface condition in organic chalcogen-source TMD epitaxy. Best results of commensurate domain growth were achieved on 1200°-O_2-annealed, 0.05°-miscut, straight-stepped Al_2O_3(0001), revealing a preferential $[11\bar{2}0]MoS_2(0001)//[11\bar{2}0]Al_2O_3(0001)$ epitaxial relationship in RHEED, and showing low, in-plane rotational twist below 2° in GIXRD Φ-scans.

This work provides fundamental understanding of large-scale synthesis of single-crystal 2D semiconductors from low-cost, low toxicity organic precursors on commercial substrates, which is highly relevant for their successful integration into industrial applications.

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