Step-edge nucleation and domain orientation control in epitaxy of transition metal dichalcogenides on sapphire

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Wafer-scale synthesis of semiconducting transition metal dichalcogenide (TMDs) monolayers is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Promising results have been demonstrated for epitaxial films deposited by vapor phase techniques such as CVD and MOCVD. However, the three-fold symmetry of TMDs such as MoS_2 and WSe_2, results in two energetically equivalent domain alignments, often referred to as 0° and 60° domains, when grown on flat high symmetry substrates such as c-plane sapphire. The oppositely oriented domains give rise to inversion domain boundaries (IDBs) upon coalescence which exhibit a metallic character and are generally undesirable. In this study, we demonstrate the epitaxial growth of unidirectional TMD monolayers on 2" diameter c-plane sapphire substrates with a significantly reduced density of inversion domains. Steps on the sapphire surface are shown to play a key role in TMD nucleation and impart a preferred orientation to the domains depending on the step edge structure and chemistry.

Metalorganic chemical vapor deposition (MOCVD) was used for the epitaxial growth of WSe_2 monolayers on c-plane sapphire, miscut ~0.2° toward the m-axis, in a cold-wall horizontal quartz-tube reactor. A three-step nucleation-ripening-lateral growth process, carried out at temperatures ranging from 850°C to 1000°C, was used to achieve epitaxial films using $W(CO)_6$ and H_2Se as precursors in a H_2 carrier gas. Density functional theory calculations demonstrate that the extent of Se passivation of the sapphire surface and the presence of oxygen remnants near the step edge are critical factors in determining the location of TMD nucleation on the step edge and the subsequent domain orientation relative to the underlying sapphire. By changing the reactor pressure, which modifies the sapphire surface via changes in the chemical potential of H and Se, the site of WSe_2 nucleation can be modified which switches the preferred orientation of the domains (Figure 1). Fully coalesced TMD monolayers are obtained with a reduced density of inversion domain boundaries (<15% areal coverage). The results demonstrate the important role of step structure and chemistry in nucleation and epitaxial growth of TMD monolayers.

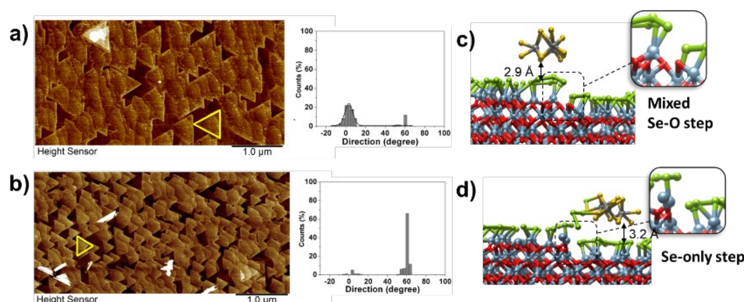

Figure 1. AFM images and histograms of WSe_2 domains grown on c-plane sapphire at (a) 200 Torr and (b) 700 Torr showing preferred orientations of 0° and 60°, respectively. Global minimum energy configuration of (c) a mixed Se-O and (d) Se-only stepped sapphire which determines the thermodynamically preferred site for nucleation.