

# Nucleation mechanisms for Chemical Vapor Deposition and Atomic Layer Deposition of 2D semiconductor materials

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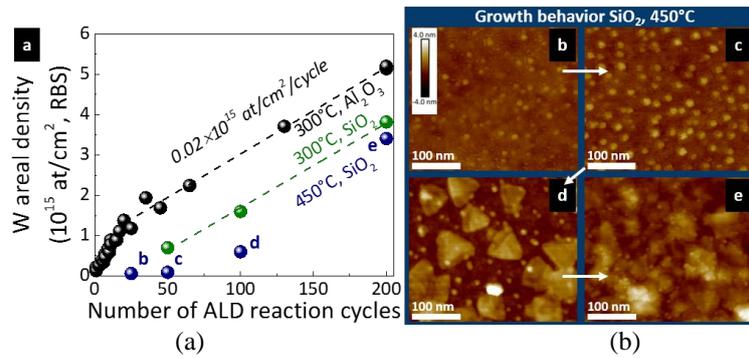
Although deposition of two-dimensional (2D) semiconductors on large area substrates has been demonstrated, there are still challenges related to achieving high quality structures and good properties for applications in nano-electronic devices [1]. Impurities, defects and crystal grain boundaries can degrade the carrier mobility in the 2D semiconductor. Precise thickness control is required as the properties can depend on the number of monolayers. In addition, applications such as monolithic 3D integrated circuits require a low thermal budget (<400°C). Different deposition techniques are possible, including chemical vapor deposition (CVD), atomic layer deposition (ALD), chalcogenidation and molecular beam epitaxy. Both “bottom up” or “top down” integration schemes exist, depending on the availability of a template for epitaxial seeding, a transfer process of the 2D material, and area selectivity in the deposition process. Deposition of monocrystalline 2D materials requires a template for epitaxial seeding. In the absence of a template, the materials are polycrystalline but one can impose a preferred growth orientation by controlling the growth kinetics. As such, CVD can provide monolayer thin 2D crystals with lateral dimensions of several micrometers. Understanding of the growth and nucleation mechanisms is not only important to control the dimensions of the 2D crystals, but it can also enable the design of area selective deposition processes.

This work discusses the nucleation and growth mechanisms of CVD and ALD of semiconducting 2D metal sulfides. We focus on metal halide precursors ( $\text{SnCl}_4$ ,  $\text{WF}_6$ ) and  $\text{H}_2\text{S}$  in view of the high potential for high purity films at mild deposition temperature and area selective deposition.  $\text{WS}_2$  and  $\text{SnS}_2$  have a layered hexagonal structure, while  $\text{SnS}$  has a double layered orthorhombic structure. The nucleation behavior depends on the precursor, starting surface (nature, number of reactive sites) and mobility of the ad-atoms and as such on the deposition temperature. This is illustrated for plasma enhanced ALD of  $\text{WS}_2$  from  $\text{WF}_6$ ,  $\text{H}_2$  plasma and  $\text{H}_2\text{S}$  [2]. A high nucleation density ensures a rapid layer closure, which occurs at a  $\text{WS}_2$  content below two monolayers for deposition on  $\text{Al}_2\text{O}_3$  at 300°C. The  $\text{WS}_2$  films are polycrystalline and highly textured but the domain size is limited (5-30nm) due to the high nucleation density. We increase the  $\text{WS}_2$  domain size to ~100nm by decreasing the nucleation density by using a less reactive substrate ( $\text{SiO}_2$ ) and higher deposition temperature (450°C) (figure 1). In addition, the versatile chemistry of  $\text{WF}_6$  enables area selective CVD processes (figure 2, [3]) and opens up opportunities for controlled seeding of 2D crystals. An even lower nucleation density and larger crystal domain size is obtained for  $\text{SnS}$  and  $\text{SnS}_2$  CVD from the  $\text{SnCl}_4$  and  $\text{H}_2\text{S}$  precursors. Depending on the deposition temperature and partial pressure of the precursors, either  $\text{SnS}_2$  or  $\text{SnS}$  is deposited. Isolated 2D crystals of several monolayers high with mainly horizontal orientation of the basal planes can be formed even when using relatively high deposition rate and low deposition temperature (400-550°C). Until layer closure, these 2D crystals preferentially grow in the horizontal direction due to a higher reactivity of the crystal edges. In contrast, as a consequence of the lack of active sites on the basal planes, the vertical growth rate is much lower. We propose a growth model that presumes that the 2D crystal height is determined by the height of the initially amorphous  $\text{SnS}_2$  islands, which crystalize only when a critical dimension (~4nm, 6 monolayers) is reached (figure 3). This insight guides the further optimization of the  $\text{SnS}_2$  and  $\text{SnS}$  CVD process to reach monolayer growth control (figure 4).

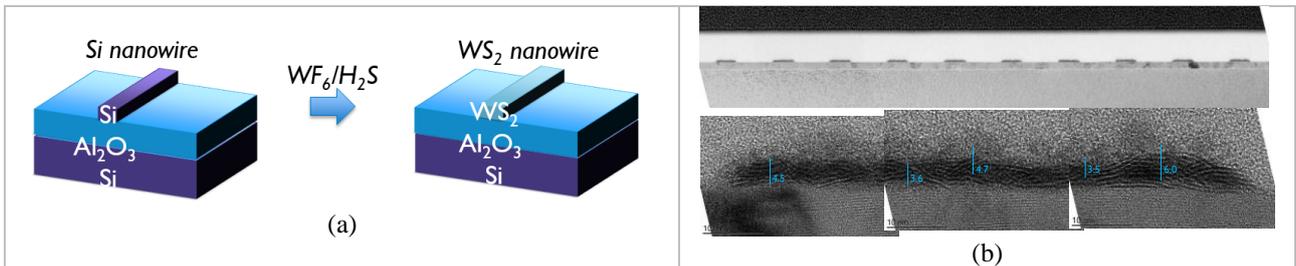
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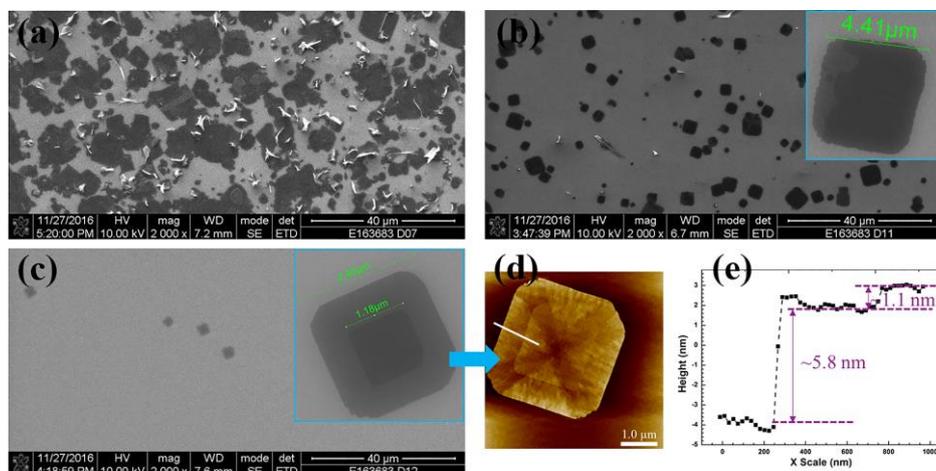
**Figure 1.** (a) Growth curves for PEALD WS<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> substrates at 300 or 400°C. The W-content was measured by Rutherford Backscattering Spectrometry (RBS). (b) Atomic Force Microscopy (AFM) for WS<sub>2</sub> PEALD on SiO<sub>2</sub> substrates with different number of cycles (b: 25 cycles, c: 50 cycles, d: 100 cycles, e: 200 cycles).



**Figure 2.** (a) Concept of area selective deposition by pre-patterned sacrificial layers, (b) Cross Section Transmission Electron Microscopy (TEM) image for area selective WS<sub>2</sub> deposition on Al<sub>2</sub>O<sub>3</sub> layers by WF<sub>6</sub>/H<sub>2</sub>S CVD at 450°C using a Si sacrificial pattern.



**Figure 3.** Schematic representation of nucleation mechanism of SnS<sub>2</sub> or SnS CVD: (a) initial nucleation of amorphous island, (b) crystallization of initial island at critical dimension, (c, d) preferential horizontal growth due to a higher reactivity of the crystal edges as compared to the horizontally arranged basal planes.



**Figure 4.** Figure (a-c): Scanning Electron Microscopy (SEM) images of SnS by SnCl<sub>4</sub>/H<sub>2</sub>S CVD at 400°C on SiO<sub>2</sub> substrates and impact of growth rate (SnCl<sub>4</sub> flow: 0.25 sccm, 0.125 sccm and 0.075 sccm, respectively). (d-e) AFM image and step height of SnS crystal for sample c.