Chemical Vapor Deposition of Monolayer-thin WS₂ Crystals from the WF₆ and H₂S Precursors at Low Deposition Temperature

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Monolayer-thin WS₂ with (0002) texture grows by chemical vapor deposition (CVD) from gas-phase precursors WF₆ and H₂S at a deposition temperature of 450 °C on 300 mm Si wafers covered with an amorphous Al₂O₃ starting surface. We investigate the growth and nucleation mechanism during the CVD process by analyzing the morphology of the WS₂ crystals. The CVD process consists of two distinct growth regimes. During (i) the initial growth regime, a fast and self-limiting reaction of the CVD precursors with the Al₂O₃ starting surface forms predominantly monolayer-thin WS₂ crystals and AlF₃ crystals that completely cover the starting surface. During (ii) the steady-state growth regime, a much slower, anisotropic reaction on the bottom, first WS₂ layer proceeds with the next WS₂ layer growing preferentially in the lateral dimensions. We propose that the precursor adsorption reaction rate strongly diminishes when the precursors have no more access to the Al₂O₃ surface as soon as the WS₂ layer completely covers the Al₂O₃ surface, and that the WS₂ crystal basal planes and AlF₃ crystals have a low reactivity for WF₆ adsorption at 450 °C. Nonetheless, a second layer of WS₂ starts to form before the first WS₂ layer completely covers the starting surface, albeit the surface coverage of the second layer is low (< 20%, after 25 minutes of CVD reaction). During the steady-state growth regime, predominantly the WS₂ crystals in the second monolayer continue to grow in lateral dimensions up to ~40 nm. These crystals reach larger lateral dimensions compared to the crystals in the bottom, first layer due to low reactivity for WF₆ adsorption on the WS₂ basal plane compared to Al₂O₃. Presumably, they grow laterally by precursor species that adsorb on and diffuse across the WS₂ surface, before being incorporated at the more reactive edges of the WS₂ crystals in the second layer. Such process proceeds slowly with only up to 40 % surface coverage of the second WS₂ layer after 150 minutes of CVD reaction. The CVD reaction is mediated by the starting surface: WF₆ precursor preferentially adsorbs on Al₂O₃, whereas adsorption is not observed on SiO₂. Nevertheless, WS₂ grows on SiO₂ in close proximity with Al₂O₃ in 90 nm pitch Al₂O₃/SiO₂ line patterns. Hence, functionalization of the starting surface (e.g., SiO₂ with Al₂O₃) can provide opportunities to grow monolayer-thin WS₂ crystals at predetermined locations by selective, lateral growth with tunable crystal size, even at low deposition temperatures.

I. INTRODUCTION

Different applications in the research domains from nanoelectronics to gas-sensing and catalysis require growth of two-dimensional (2D) transition metal dichalcogenides (MX_2 , with M a transition metal and X a chalcogen) by manufacturable deposition techniques^{1–5}. The structure and properties of the MX_2 layers need to be tailored according to the desired application. To reach the desired crystalline structure and properties for each application, fundamental understanding about the growth process by such deposition techniques is needed.

The majority of the synthetic MX_2 materials are grown by chemical vapor deposition (CVD) and chemical vapor transport (CVT). In CVT, precursors are used in a furnace at moderate to high deposition temperatures ($650\text{ }^\circ\text{C} - 1150\text{ }^\circ\text{C}$)^{6–9}. Such deposition processes can yield monolayer-thin crystals with lateral dimensions beyond micrometers. Uniformity and continuity of the MX_2 layers on large area substrates can be achieved, provided that the precursors can be delivered in a controllable, repeatable way across the wafer surface using dedicated precursor delivery system^{10,11}. The number of layers can be controlled by carefully tuning the reaction kinetics during growth processes, e.g., by adapting metal and chalcogen precursor partial pressure and deposition temperature. Few groups have investigated the nucleation of molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) grown by CVD using both halide (e.g., molybdenum pentachloride MoCl_5) and metalorganic (e.g., molybdenum and tungsten hexacarbonyl $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$) precursors^{10–13}. A layer-by-layer growth mode can be established where the second layer starts to grow only when the first layer completely covers the starting surface. Most of the reported processes in literature, proceed at moderate to high deposition temperatures ($\geq 550\text{ }^\circ\text{C}$). By limiting the deposition temperature, MX_2 materials can be directly implemented in temperature sensitive structures, without the need for a material transfer, for example back-end-of-line (BEOL) structures or organic materials. However, the nucleation mechanisms during CVD processes at low deposition temperature are currently not understood, albeit they are essential to control the structure and properties of 2D materials and hereby tailor the material properties towards specific applications.

In this work, we have investigated the growth and nucleation mechanism of WS_2 CVD from tungsten hexafluoride (WF_6) and dihydrogen sulfide (H_2S) at low deposition temperatures ($200\text{ }^\circ\text{C} - 450\text{ }^\circ\text{C}$)¹⁴. We show that monolayer-thin WS_2 crystals can be grown on an amorphous Al_2O_3 starting surface. We explore the deposition window for the CVD process by investigating the influence of precursor partial pressure ratio and deposition temperature on the 2D structure and crystallinity of the deposited WS_2 . We analyze how the amount of deposited WS_2 evolves with deposition time for the CVD process at $450\text{ }^\circ\text{C}$. We study the nucleation mechanism by analyzing the morphology of the WS_2 crystals and propose a model for the nucleation behavior. Finally, we illustrate that the CVD reaction strongly depends on the reactivity of the starting surface

towards the CVD precursors by comparing two starting surfaces that have different reactivity, i.e. amorphous Al₂O₃ and SiO₂. In that context, we investigate the possibility to functionalize SiO₂ using an ALD reaction cycle of Al₂O₃ in order to enable the nucleation of WS₂ on SiO₂, and evaluate the inherent selectivity of the CVD process in 90 nm pitch Al₂O₃/SiO₂ line patterns.

II. EXPERIMENTAL SET-UP

WS₂ layers are grown by CVD from WF₆ and H₂S (99.9 % pure H₂S, 10 % in He) in a hot-wall, shower-head type plasma enhanced (PE) CVD chamber connected to an ASM deposition platform Eagle12. The susceptor temperature is varied between 200 °C and 450 °C. Wall and showerhead temperature were fixed at 185 °C and 225 °C, except for the susceptor temperature of 200 °C, in which case the temperatures were decreased to 175 °C and 200 °C, respectively. The reactor pressure is kept constant at 2 Torr. During the CVD reaction, 5 sccm of WF₆ and 695 sccm of H₂S flow through the chamber for partial pressures of $\sim 9 \times 10^{-3}$ Torr and $\sim 1.2 \times 10^{-1}$ Torr, respectively.

WS₂ is grown on 300 mm Si substrates covered with a 30 nm amorphous Al₂O₃. The amorphous Al₂O₃ layer is grown by atomic layer deposition (ALD) from trimethyl aluminum (TMA) and water (H₂O) at 300 °C in a hot-wall, cross-flow type ASM Pulsar 3000 reactor. All substrates are stabilized in the PECVD reactor under N₂ for 5 minutes prior to WS₂ CVD.

The areal density of deposited W and S is measured by Rutherford backscattering spectroscopy (RBS) using a 1.52 MeV He⁺ ion beam and with the detector placed at a scattering angle of 170 °¹⁵. The compositional ratio (i.e., S/W ratio) is calculated from the measured areal densities. X-ray photoelectron spectroscopy (XPS) describes the chemical bonding nature and chemical purity of WS₂ on the Al₂O₃ starting surface, using a Theta300 system from Thermo Instruments with a monochromatized Al K α X-ray source (1486.6 eV) and a spot size of 400 μ m. Peaks are fitted using pseudo-Voigt functions (unless mentioned otherwise), after referencing to the C1s peak and correcting for Shirley background. The F coverage (in atoms/cm²) on the Al₂O₃ surface during the CVD reaction is calculated from the F1s spectrum relative to Al2s using a limiting case of the standard overlayer/bulk intensity ratio model by Petrovykh et al.,

$$n_F = (I_F / I_{Al_2O_3}) \cdot \cos(\Theta) \cdot \lambda_i \cdot N_{Al_2O_3} \quad (1)$$

with n_F the coverage of the adsorbed F (in atoms/cm²), I_F and $I_{Al_2O_3}$ are the measured intensities of adsorbed F (from F1s) and Al (from Al2s) in Al₂O₃ surface at exit angle Θ of 22 ° (w.r.t. surface normal) respectively, λ_i the electron inelastic mean free path (IMFP) in Al₂O₃ (i.e., 3.04 nm for 1486.6 eV electron kinetic energy) calculated using the TPP-2M equation by Tanuma et al. and the NIST Electron Effective Attenuation Length Database, and $N_{Al_2O_3}$ the atomic concentration in the substrate

$(1.88 \times 10^{22} \text{ atoms/cm}^3)^{16-18}$. In this limiting case, the F coverage is assumed sub-monolayer neglecting signal attenuation in the F overlayer. Therefore, calculated areal densities serve only as indication and estimation of the adsorbed F content since the model does not take into account how the signal is attenuated by the distribution of the overlayer across the Al_2O_3 surface: i.e., discrete (e.g., for agglomerates or 3D islands) or continuous. Furthermore, angle-resolved (AR-) XPS is used to investigate the 90 nm pitch nanoscale $\text{Al}_2\text{O}_3/\text{SiO}_2$ line patterns. When the photoelectrons are collected at sufficiently large exit angles with respect to the normal on the sample surface (i.e., $\geq 45^\circ$ for the line pattern dimensions used in this study), the individual contribution from the SiO_2 lines can be isolated from the Al_2O_3 areas.

The grain size and morphology, and root-mean square (RMS) roughness of the WS_2 layer is characterized by atomic force microscopy (AFM) using a Nanoscope V instrument from ICON PT (Bruker) in tapping mode. Grain size is extracted from the AFM images by watershed segmentation using *Gwyddion* analysis software¹⁹. Grain boundaries are determined based on the local minima across the surface by shedding virtual water droplets across the surface (see Figure S1, *Supplementary Material*). By controlling the droplet size and number of iterations in the watershed algorithm, individual crystals are approximated. Grain size is defined as the diameter of the disc with equivalent projected surface area. Crystal density and surface coverage are extracted therefrom. Height of the individual crystals, i.e., the number of layers, is determined from the corresponding height distribution profile. In order to collect sufficient statistics on the grain size, surface coverage and crystal density, four individual atomic force micrographs (500 nm by 500 nm) for more than 2000 crystals are analyzed for each deposition condition.

In addition, the WS_2 and AlF_3 crystals are analyzed by plan-view and cross-sectional transmission electron microscopy (TEM), respectively. In plan-view observation, a FEI TITAN electron microscope is used operating at 60 kV to minimize the electron beam induced damage to the WS_2 , whereas cross-sectional TEM is performed using a FEI Tecnai F30 electron microscope operating at 300 kV. For plan-view observation, the WS_2 is transferred from the growth substrate to a carbon lacey TEM grid, with more details on the transfer procedure mentioned elsewhere²⁰. To visualize the AlF_3 islands, they are embedded in an eC capping layer and Pt cap. Their elemental composition is determined by energy dispersive X-ray analysis (EDS).

Raman and photoluminescence (PL) spectroscopy are used to further investigate the structure of the WS_2 layers. Horiba Jobin-Yvon HR800 Raman instrument is operating with a 532 nm laser excitation wavelength, at ~ 2 mW laser power and $1 \mu\text{m}^2$ spot size. A 300 μm confocal hole with a 1800 gr/mm grating is used. Laser exposure time is limited to 200 s, to minimize laser induced damage to the WS_2 layers. After background correction by blanket Si referencing, the individual Raman modes are de-

convoluted using a Voigt fitting profile. PL response is fitted using Gaussian profile. For peak assignment and fitting of CVD WS₂, reader is referred to *Supplementary Material* and to our earlier work²⁰.

III. RESULTS AND DISCUSSION

The paper is organized in four sections. *Section A* explores the influence of deposition temperature and precursor partial pressure ratio on the structure and crystallinity of the WS₂ layer. WS₂ crystals grow by simultaneous exposure of WF₆ and H₂S to amorphous Al₂O₃. *Section B* describes the growth evolution of the WS₂ CVD by RBS at a fixed deposition temperature of 450 °C, and proposes a model for the reaction mechanism. *Section C* identifies the growth mode during the CVD process by analyzing the morphology of the WS₂ crystals by AFM and TEM, and proposes a model for the nucleation of the WS₂ crystals. Finally, *section D* alleviates our understanding of the growth mechanism during the CVD reaction by comparing how the dependence on the starting surface evolves from blanket to nanoscale patterns.

A. WS₂ deposition by CVD from WF₆ and H₂S: process window

Simultaneous exposure of the WF₆ and H₂S precursors to an amorphous Al₂O₃ starting surface enables WS₂ deposition in a temperature window between 250 °C and 450 °C (**Figure 1a**). The CVD process can proceed according to the following overall reaction equation (1).

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All WS₂ depositions were performed with a precursor partial pressure ratio H₂S/WF₆ of ~14, using a partial pressure of WF₆ and H₂S of $\sim 9 \times 10^{-3}$ Torr and $\sim 1.2 \times 10^{-1}$ Torr, respectively. A total deposition time of 4 hours is used to ensure that the steady-state growth regime is reached for all deposition temperatures, unless mentioned otherwise.

The S/W ratio remains constant within that temperature window, from (1.9 ± 0.2) at 250 °C to (2.0 ± 0.2) at 450 °C

FIG. 1. (color online) (a) W areal density and S/W ratio measured by RBS as a function of the deposition temperature for CVD WS₂ on amorphous Al₂O₃ starting surface after 4 hours deposition time. The uncertainty on W areal density varies around 3%, rendering the error bars undistinguishable by eye from the data points; (b) W4f XPS spectrum of WS₂ CVD at 450 °C on amorphous Al₂O₃ after 2 h 30 min deposition.

At a lower deposition temperature (200 °C), WS₂ is not formed (**Figure 1a**). Much less W is deposited [$(0.42 \pm 0.02) \times 10^{15}$ W atoms/cm²] and no S is detected by RBS (detection limit of $> 2 \times 10^{14}$ S atoms/cm²). This suggests that the WF₆ adsorption reactions occur slower at 200 °C. In addition, the partial reduction of W from the +VI oxidation state in WF₆ to the +IV oxidation state in WS₂ by H₂S might require temperatures higher than 200 °C. The amount of deposited W and S after 4 hours of deposition time remains constant throughout the 250 °C – 450 °C temperature window (**Figure 1a**). This might suggest that the CVD process is self-limiting, which will be investigated in section B.

Polycrystalline WS₂ layers with (0002) texture, i.e., basal plane orientation parallel to substrate surface, are obtained between 250 °C and 450 °C. For a fixed deposition time, the size of the WS₂ crystals depends on the deposition temperature. At 250 °C and 300 °C, the WS₂ grain size is limited to ≤ 20 nm for 4 hours of CVD reaction (**Figure 2a**, AFM). The negligible photoluminescence intensity falls in line with a poor structural quality and small grain size of the WS₂ crystals (**Figure 2b**).

By increasing the deposition temperature up to 450 °C, the WS₂ domain size expands up to 40 nm for a deposition time of 150 minutes (**Figure 2c**). The crystals have a comparatively stronger photoluminescence response, with corresponding full width at half-maximum (fwhm) of ~0.08 eV, compared to 0.04 eV – 0.075 eV for exfoliated and synthesized WS₂ (**Figure 2b**)^{21–24}. This confirms the improvement of structural quality of the WS₂ crystals by increasing the deposition temperature. Furthermore, it indicates the formation of few-monolayer-thin WS₂ crystals, as the PL yield is known to decrease and eventually disappear with increasing number of layers (i.e., towards bulk) due to a transition from direct to indirect bandgap²⁵. In addition, the Raman response strengthens and the fwhm of the longitudinal acoustic phonon mode (2LA[M]) narrows to ~12.5 cm⁻¹ when the deposition temperature increases (see *Supplementary Material*)²⁶.

FIG. 2. (color online) (a) Atomic force micrograph (500 nm × 500 nm) of CVD WS₂ at deposition temperature of 300 °C; (b) PL spectra of as-grown CVD WS₂ for a series of deposition temperatures between 200 °C and 450 °C; and (c) Atomic force micrograph of CVD WS₂ at deposition temperature of 450 °C. All WS₂ layers are grown on amorphous Al₂O₃ for a fixed deposition time of 4 hours. The lateral scale bars (inset, white) of the atomic force micrographs are set to 100 nm. The height scale is fixed from 0 nm to 3 nm.

The structure of the WS₂ crystals deposited at 450 °C is further investigated by plan-view TEM. In the plan-view observation along [0001] crystal direction, WS₂ appears as monolayer-thin and continuous as it is suspended across and beyond the 1 μm-wide holes in the carbon lacey TEM grid (**Figure 3a**). In absence of a template for epitaxial seeding, the crystals are randomly oriented along [0001] axis (**Figure 3b**). The bottom, single layer is continuous and consists of a trigonal prismatic lattice, and the grain boundaries of the WS₂ crystals are clearly distinguishable (**Figure 3c**). Based on the difference in contrast

in the scanning transmission micrographs, locally a second and occasional third layer appear, but their surface coverage is limited ($\leq 20\%$) (**Figure 3a,b,d**). The second layer can grow in two ways. On the one hand, the next WS_2 layer nucleates from a grain boundary in the first single WS_2 layer, and starts to overgrow the neighboring grains in that first layer giving rise to Moiré patterns as the grains are randomly rotated along $[0001]$ crystal axis (**Figure 3d**). The regions with Moiré patterns across the second layer are marked in red, with the red dotted lines highlighting the grain boundaries in the bottom, first single layer. On the other hand, the second layer can also grow in registry with the underlying WS_2 layer by epitaxial seeding on that bottom WS_2 layer. The lateral dimensions of the WS_2 crystals nucleating on the basal plane of the first single layer vary between 5 nm and 40 nm (see *Supplementary Material*, Figure S2). Vacancies and defects appear in the WS_2 monolayer during the TEM observation. Some of these defects can form during the water-based transfer of the CVD grown layers from the Al_2O_3 starting surface to the TEM grid, e.g., defects near the more fragile WS_2 grain boundaries. Such defects enlarge during the TEM observation as a result of the repeated electron beam exposure, despite lowering the electron beam energy to 60 kV to minimize the generated damage to the 2D layer.

As it has been shown that the M/X precursor partial pressure ratio in CVD can affect the morphology and size of MX_2 crystals, we have explored the impact of the $\text{H}_2\text{S}/\text{WF}_6$ partial pressure ratio (between 0.5 and 14) in the WS_2 CVD process at 450°C ^{11,24}. However, this did not reveal a significant influence on the morphology and size of the deposited WS_2 crystals. Therefore, throughout the remainder of our investigation, we fixed the $\text{H}_2\text{S}/\text{WF}_6$ partial pressure ratio at 14.

FIG. 3. (color online) Scanning transmission micrographs in plan-view observation of monolayer WS_2 grown by CVD from WF_6 and H_2S for 150 minutes at 450°C on amorphous Al_2O_3 . The orientation of the WS_2 grains along $[0001]$ crystal direction is random. The large, bright patterns on the low magnification image in (a) correspond to the C-support film of the carbon lacey TEM grid on which the WS_2 is transferred,

and demonstrate that the WS₂ layer is continuous and originally completely covered the Al₂O₃ starting surface. (b) Majority of the WS₂ crystals are monolayer-thin, with locally the onset of second and occasional third layer as indicated by the change in intensity (i.e., contrast). (c) Atomic resolution micrograph of single layer WS₂, with trigonal prismatic lattice coordination and appearance of grain boundaries. (d) Onset of second layer nucleating on the basal plane of the bottom, first WS₂ layer. Grain boundaries of the bottom single WS₂ layer are highlighted by red dotted lines to guide the eye. The red dotted lines also mark the regions of the second layer where Moiré patterns appear as a result of random rotation with respect to the underlying layer along [0001] axis. The second WS₂ monolayer covers about ~20% of the surface of the underlying first monolayer, as extracted from the transmission micrographs.

B. Growth evolution of WS₂ CVD on amorphous ALD Al₂O₃ at 450 °C

In this section, the growth behavior of the WS₂ CVD process from WF₆ and H₂S on the amorphous Al₂O₃ surface is investigated. We analyze the amount of deposited WS₂ as a function of the deposition time at a fixed deposition temperature of 450 °C and partial pressure ratio of 14.

WS₂ is formed by a CVD process that consists out of two distinct growth regimes: i.e., the initial and steady-state growth regime.

First, a fast and self-limiting reaction with the Al₂O₃ starting surface leads to the formation of monolayer-thin WS₂ crystals, and AlF_x crystals during the initial growth regime (**Figure 4**). During the first 25 minutes, the amount of deposited WS₂ gradually increases to $(1.17 \pm 0.02) \times 10^{15}$ W atoms/cm² (RBS). This is the equivalent amount of ~1 WS₂ ML, as a fully dense and crystalline WS₂ layer consists of 1.16×10^{15} W atoms/cm².

Second, the WS₂ deposition proceeds much slower on this formed, first WS₂ monolayer with only an incremental increase in the amount of deposited WS₂ during the steady-state growth regime (RBS, **Figure 4a**). After 25 minutes of CVD, the amount of deposited W and S starts to saturate, and the WS₂ content increases only slightly, indicating a second slower growth component in the CVD process. After 24 hours of WF₆ and H₂S exposure, the deposited amount of WS₂ is $(1.48 \pm 0.03) \times 10^{15}$ atoms/cm², the equivalent of ~1.3 ML of WS₂.

Simultaneously with the growth of WS₂, the Al₂O₃ surface gets partly covered by F. Already after 1 minute of CVD reaction, 3.3×10^{15} F atoms/cm² are deposited in addition to the nucleation of WS₂ (XPS). The XPS F1s spectrum illustrates the F atoms are bonded to Al (**Figure 4b**), and that F primarily locates at the top surface of the Al₂O₃ layer (AR-XPS, not shown). The surface fluorination appears also to be self-limiting as the amount of F deposited shows signs of saturation (**Figure 4a**). Note that the exact quantification of the F areal density by XPS is complicated by how the F is distributed across the surface (e.g., geometrical constraints).

FIG. 4. (color online) (a) Growth curve of CVD WS₂, with W and S areal density by RBS, F areal density by XPS (primary vertical axis) and the S/W ratio (RBS, secondary vertical axis) as a function of the deposition time (in hours, primary horizontal axis) and WF₆ exposure (in Langmuir, L, secondary horizontal axis) at 450 °C on 30 nm amorphous Al₂O₃. The uncertainty on W areal density varies around 3%, rendering the error bars undistinguishable by eye from the data points; (b) F1s XPS spectra of amorphous Al₂O₃ surface (bottom) and after 60 s of WF₆ and H₂S exposure to amorphous Al₂O₃ surface (top). The inorganic-F represents clean room standard fluorine-containing contaminants on the bare Al₂O₃/Si sample surface, which can include contaminant species ranging from metal-fluorides to silicon-fluorides.

During the initial growth regime, the WS₂ and AlF_x species are considered to form primarily through surface reactions since the amount of deposited WS₂ strongly diminishes as soon as the Al₂O₃ starting surface becomes completely covered. The WF₆ precursor adsorption rate is mainly determined by the available number of reactive surface sites. The areal density of reactive surface sites is comparatively larger on the Al₂O₃ starting surface, due to the presence of aluminol (Al–OH) and aluminoxane (Al–O–Al) bridges²⁷. In contrast, the self-passivating WS₂ crystals are far less reactive towards the CVD precursors. The reaction between WF₆ and Al₂O₃ is predicted to be exothermic with a reaction enthalpy ΔH of - 111 kcal/mol for the overall reaction equation (3), according to literature²⁸.

WF_6 can react through ligand-exchange reaction, e.g., by proton transfer with hydroxyl groups according to reaction (4). Alternatively, WF_6 undergoes dissociative adsorption on the Al_2O_3 , according to reaction (5). These proposed reactions can also describe the fluorination of the Al_2O_3 starting surface: through dissociative adsorption of WF_6 , or indirectly through reaction with HF , a reaction product of the CVD process^{29,30}. Simultaneously, the H_2S precursor can react with the adsorbed $-\text{W}^{6+}\text{Y}$ surface species through a cascade of intermediate reactions that enable the partial reduction of the W atom from +VI in WF_6 to +IV in WS_2 , according to reactions (6-7). The CVD precursors are considered to be thermally stable at the investigated deposition temperatures. The thermal decomposition temperature of WF_6 is reported to be 750 °C and H_2S is considered thermally stable at temperatures < 500 °C^{31,32}. Therefore, both WF_6 and H_2S are assumed to arrive intact at the Al_2O_3 starting surface

During the steady-state growth regime, the WF_6 and H_2S precursors are considered to react primarily through surface reactions according to (8). Although gas-phase reactions cannot be excluded, the WS_2 CVD process is strongly mediated by reaction on the surface through the available reactive surface species. That is, as soon as the Al_2O_3 starting surface gets completely covered by the inherently less reactive WS_2 and AlF_x , the amount of deposited WS_2 increases only marginally with deposition time (**Figure 4.a**). Therefore, we propose that both WF_6 and H_2S can physically adsorb on the WS_2 surface, and migrate across that surface until a reactive site is encountered where a surface reaction can occur. In that context, the low steady-state growth rate either results from the few available reactive sites on the WS_2 surface, or from kinetically or thermodynamically limited surface reactions at the investigated deposition temperatures.

The underlying redox mechanism cannot be revealed from the current study and requires a more detailed mechanistic study.

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C. Structure and morphology of WS₂ crystals

Next, we analyze how the structure and morphology of as-deposited WS₂ and AlF_x evolves as a function of the deposition time. In addition to the amount of deposited material from RBS and XPS (**Figure 4**), we investigate the surface coverage, crystal density, and crystal grain size and height by AFM (**Figure 5,6**). Additional structural information was provided by TEM (**Figure 3, 7**), and Raman spectroscopy and PL (**Figure 8**). All experimental observations will be combined to develop a model for the nucleation behavior of the WS₂ CVD process.

During the first minute of the CVD process, isolated and monolayer-thin WS₂ nuclei are formed on the Al₂O₃ surface (**Figure 5**, AFM). Only ~6 % of the surface is covered with WS₂ for about $(7 \pm 1) \times 10^{13}$ W atoms/cm², while the amount of F is much higher, i.e. 3.3×10^{15} F atoms/cm². The Al₂O₃ surface is mostly covered with a rather uniform AlF_x layer, as the peak-to-valley height is low (~1.0 nm) and the RMS roughness remains constant: i.e., ~0.16 nm RMS, compared to 0.16 nm RMS for the untreated Al₂O₃ surface (**Figure 5a, 6a**). Assuming that a fully dense and crystalline tetragonal κ -AlF₃ is composed out of 7.5×10^{14} Al atoms/cm², about ~1.5 ML of AlF₃ covers almost 95 % of the Al₂O₃ surface. This suggests that F covers the surface rather homogeneously during this initial growth regime. In addition, the small WS₂ nuclei form simultaneously.

FIG. 5. (color online) Atomic force micrographs ($500 \text{ nm} \times 500 \text{ nm}$) during CVD growth of WS_2 at different deposition times for (a) 1, (b) 10, (c) 25, (d) 50 and (e) 150 minutes. WS_2 is deposited at 450°C on amorphous Al_2O_3 . The lateral scale bars (inset, white) of the atomic force micrographs are set to 100 nm . The height scale is fixed from 0 nm to 3 nm .

With increasing deposition time, the topography of the surface changes significantly, resulting in an increase in roughness (**Figure 6a**). The surface coverage of WS_2 increases as the CVD process proceeds (**Figure 6b**). After 10 minutes of CVD, up to 70 % of the Al_2O_3 surface is covered with WS_2 crystals with grain sizes between 5 nm and 20 nm (**Figure 6b,c**). Note that during this initial growth regime, the WS_2 crystals are monolayer-thin, albeit a small fraction of WS_2 crystals does have already the onset of a second layer (**Figure 6d**). It remains unclear yet how the second and third layer nucleate on the first WS_2 layer. Presumably, they form during the initial growth regime, when the Al_2O_3 starting surface is still partly accessible. They can continue to grow during the CVD reaction by precursor adsorption on and diffusion across the surface of the first and second WS_2 monolayer. Such process is expected to proceed slowly in view of the low sticking probability of WF_6 on WS_2 surface ($< 1 \%$, assuming average WS_2 crystal grain size of 10 nm) due to the unreactive and self-passivating nature of the WS_2 basal plane (**Figure 3**). Alternatively, these crystals ripen during the CVD reaction by a sintering mechanism.

FIG. 6. (color online) (a) WS_2 crystal density (in green) and RMS surface roughness (in black) as a function of the CVD deposition time; (b) Surface coverage of WS_2 and AlF_3 crystals as a function of deposition time. Error bars are not visible on the graphs of (a) and (b), but vary between $\pm 1\%$ and $\pm 3\%$. Dotted lines are a guide for the eye; (c) Box plot of WS_2 crystal grain size and (d) corresponding height distribution for a discrete series of deposition times (inset). WS_2 is deposited at 450°C on an amorphous Al_2O_3 surface.

Simultaneously with the formation of the 2D WS_2 crystals, much higher islands grow in a 3D growth mode, and reach lateral and vertical dimensions of up to 40 nm and 20 nm, respectively (**Figure 5**, i.e., white islands in AFM). TEM and EDS reveal that these islands are tetragonal AlF_3 crystals (**Figure 7**), consistent with the presence of F. The majority of the AlF_3 crystals correspond to the tetragonal $\kappa\text{-AlF}_3$ phase and are (200) textured, with corresponding lattice spacing a of 0.570 nm (**Figure 7a–c**, FFT pattern)³³. The amount of F appears to remain constant after the first minute of the CVD process (**Figure 4**). This implies that considerable reorganization occurs of the initially smooth AlF_x layer, that agglomerates into 3D AlF_3 crystals. The surface fraction of AlF_3 can be determined by AFM by assuming that all crystals with height exceeding 2.5 nm, i.e., the equivalent of 4 ML of WS_2 , correspond to AlF_3 . Such approximation is justified as only a negligible percentile fraction of WS_2 crystals exceeds 4 ML (**Figure 6d**). The surface coverage of AlF_x substantially decreases to $\sim 8\%$ after 25 minutes of CVD (**Figure 6b**). Thus, the WS_2 surface coverage increases with deposition time, while the AlF_3 surface coverage decreases because of the agglomeration process. This process continues until the steady-state growth regime is reached.

FIG. 7. (color online) (a) Scanning micrograph of CVD WS_2 and 3D AlF_3 crystals covering the amorphous Al_2O_3 . (b) High-angle annular dark field scanning transmission micrograph and (c) bright field cross-sectional transmission micrograph of 3D AlF_3 crystal. Note the

roughening of the Al_2O_3 surface underneath the AlF_3 crystal in (b); and elemental EDS mappings of (d) Al, (e) F, (f) W and (g) S, identifying that the 3D islands primarily consist out of Al and F. WS_2 is deposited at 450 °C for 25 minutes on amorphous Al_2O_3 .

After 25 minutes of CVD reaction, the amount of deposited WS_2 starts to saturate (**Figure 4**). At that point, the WS_2 surface coverage is ~90 %, and it saturates as well (**Figure 6b**). Indeed, as the amount of deposited WS_2 increases only incremental, the surface coverage is expected to remain constant during the steady-state growth regime. From AFM, the continuation of the WS_2 layer underneath the AlF_3 crystals cannot be distinguished, and therefore this needs to be taken into account when interpreting the extracted surface coverages (**Figure 6b**). It remains unclear if the WS_2 forms a continuous layer across the Al_2O_3 starting surface with the AlF_3 crystals residing on top of the WS_2 basal plane, or if the AlF_3 crystals are incorporated in the bottom, first WS_2 layer.

Nevertheless, the WS_2 crystals continue to grow in the lateral dimensions even during the steady-state growth regime (**Figure 6c**). After 25 minutes, about 13 % of the WS_2 crystals is larger than 20 nm in lateral dimensions, whereas after 150 minutes up to 40 % of the WS_2 crystals is larger than 20 nm. In addition, the crystal density decreases as a function of deposition time (**Figure 6a**), whereas the surface coverage of the bottom, first WS_2 layer remains constant during the steady-state growth regime. To elucidate the governing nucleation mechanism that can explain the increase in crystal grain size during the steady-state growth regime, we have monitored the evolution of the crystal grain size distributions (GSDs) as a function of deposition time (see Figure S2,S3, *Supplementary Material*). In fact, from that GSD evolution, predominantly the WS_2 crystals in the second layer continue to expand in the lateral dimensions, as the WS_2 crystals in the second layer take up the largest portion of the right-hand side of the GSD (see Figure S3, *Supplementary Material*). Moreover, the surface coverage of the second layer increases further during the steady-state growth regime, from ~20 % after 25 minutes to up to 40% after 150 minutes of CVD reaction. The increase in the surface area covered by WS_2 crystals in the second layer is in agreement with the absolute amount of deposited W and S during the steady-state growth regime, as determined by RBS (**Figure 4a**).

The growth of the crystals in the second (and occasional third) layer on the bottom, first WS_2 layer can a priori proceed by several possible mechanisms as mentioned earlier, each of which are discussed below. First, the second layer can start to grow underneath the existing monolayer-thin WS_2 crystal domain, by reaction with the Al_2O_3 surface at the boundaries between the WS_2 grains. Such mechanism in analogy to graphene growth on catalytic metal surfaces (e.g., Ni), where a second graphene layer can start growing underneath the preexisting single layer graphene domain, is not supported by TEM in this study (**Figure 3**)³⁴.

Second, the crystals in the second and third layer can grow by a crystal ripening mechanism, albeit so far, we were not able to discern any ripening mechanism during the steady-state growth regime. Generally, two types of crystal ripening processes can be encountered during CVD processes: Ostwald ripening or Smoluchowski aggregation. During Ostwald ripening, crystals ripen by atomic diffusion processes, whereas during Smoluchowski aggregation clusters of atoms diffuse across the surface, followed by agglomeration^{35–37}. In both cases, the WS₂ crystal grains can grow in the lateral dimensions with deposition time even though no additional WS₂ is deposited. However, interrupting the CVD reaction after 50 minutes, and annealing the as-deposited WS₂ in H₂S ambient –without providing WF₆ precursor– did not reveal significant change in the GSD (see Figure S4, *Supplementary Material*). This suggests that crystal ripening mechanisms do not play a dominant role during the CVD reaction, as no clear evolution in the GSD is observed during the annealing period. More detailed experiments would be required to investigate the contribution from crystal ripening processes during the CVD reaction.

Therefore, we propose that these crystals grow by precursor adsorption on and diffusion across the WS₂ surface, followed by incorporation of mobile precursor species at the more reactive edges of the WS₂ crystals in the second layer. However, the lateral growth of the crystals in the second layer is anticipated to proceed extremely slow in view of the low WF₆ precursor adsorption rate on the WS₂ surface, due to the unreactive and self-passivating nature of the WS₂ basal plane. This explains the slow surface coverage of the second WS₂ layer across the bottom, first WS₂ layer during the CVD reaction. In addition, this difference in reactivity of the WF₆ adsorption on the Al₂O₃ starting surface and the WS₂ layer, also clarifies the fast and slow growth component that is observed in the CVD growth curve during the initial and the steady-state growth regime, respectively (RBS, **Figure 4**).

The WS₂ Raman and PL response increase with total deposition time in the steady-state growth regime, further confirming the structural improvement and lateral growth of the WS₂ crystals. In Raman, the full width at half-maximum (fwhm) of the prominent 2LA(M) mode is $\sim 12.5 \text{ cm}^{-1}$ during the steady-state growth regime (**Figure 8a**), which is comparable to values reported for other CVD processes and approaches the fwhm for exfoliated WS₂ crystals of $(8.9 \pm 0.5) \text{ cm}^{-1}$ (see Figure S5, *Supplementary Material*)²⁶. Despite the nanocrystalline grain structure and random in-plane orientation of the grains, such values for the fwhm of the 2LA mode might suggest that the atoms are well-ordered within a single grain along (0001). The structural improvement of the WS₂ crystals in the first and/or second layer in the steady-state CVD growth regime, is also indicated by the increasing PL signal (**Figure 8b**). After 10 minutes of CVD reaction, the deposited WS₂ does not appear to be PL active. However, when the crystals start to grow preferentially in the lateral dimensions during the steady-state growth regime, the PL response increases with deposition time. The fwhm of the PL response approaches $\sim 0.08 \text{ eV}$, close to the values reported for exfoliated and synthesized WS₂ in literature ($0.04 \text{ eV} - 0.075 \text{ eV}$)^{21–24}.

FIG. 8. (color online) (a) Raman and (b) PL spectra of the CVD WS₂ crystals as a function of deposition time. Red lines indicate fitting profile based on Voigt (Raman), and Gaussian (PL) functions, respectively. WS₂ is deposited at 450 °C on amorphous Al₂O₃. For more details on the used fitting profile, the reader is referred to the *Supplementary Material*.

The PL response is typically a fingerprint for monolayer-thin WS₂ (**Figure 8b**), since the PL intensity sharply decreases from single layer to multi-layer WS₂ due to a transition from direct to indirect bandgap^{21,22}. Indeed, AFM confirms that up to 70 % of the as-deposited WS₂ crystals are one monolayer high (**Figure 6d**), in agreement with TEM observation (**Figure 3**). Raman also indicates that the WS₂ crystals mainly remain monolayer-thin since the difference in peak position between the 2LA(M) and A_{1g}(Γ) mode remains constant around ~66.6 cm⁻¹ (see *Supplementary Material*). This difference in peak position is in close agreement with values reported for monolayer exfoliated and synthesized WS₂ of 66.1 cm⁻¹ and (66.4 ± 0.5) cm⁻¹³⁸. Nevertheless, a minor fraction of the WS₂ crystals develop the onset of a second and third layer (**Figure 6d**). The fraction of crystals that consists out of more than a monolayer increases with deposition time from ~20 % after 25 minutes to ~30 % at 150 minutes, confirming that even the second and third layer can continue to grow laterally.

Apart from the nucleation mechanism of the WS₂ crystals, the 3D AlF₃ crystals likely form by a type of crystal ripening mechanism, such as Ostwald ripening or Smoluchowski aggregation. During the initial growth regime (i.e., first 25 minutes), the morphology of AlF_x surface species drastically changes with AlF_x species migrating on top of the growing WS₂ surface, where they eventually agglomerate into larger 3D crystals. Note that AlF₃ crystals are not observed in plan-view TEM, as the crystals are soluble in water used to transfer the WS₂ from the starting surface to the TEM grid (0.559 g / 100 mL at 25 °C)³⁹.

The AlF_x migrates by atomic or cluster diffusion processes through either surface diffusion, or gas-phase diffusion (e.g., by re-deposition of volatile aluminum sub-fluoride species), or through a combination of both. In the first case, i.e., AlF_x ripening by surface diffusion, the lowering of the surface free energy could be the driving force behind the surface diffusion of AlF_x. However, the surface energies of AlF₃ and amorphous Al₂O₃ are fairly comparable, at 0.85 J/m² and (0.97 ± 0.04) J/m², respectively, compared to 0.04 J/m² for WS₂^{40–42}. Hence, there is no thermodynamic driving force for surface diffusion of AlF_x to lower the surface energy of the growing surface. In the second case, AlF_x migrates by gas-phase diffusion. The formation of volatile aluminum subfluorides is observed by two independent studies at comparable deposition temperatures (i.e., up to 450 °C) by exposing an Al starting surface to WF₆, albeit at much smaller dose of WF₆ (100 L compared to > 10⁶ L in this study)^{29,30}. Volatile AlF_x surface species might form through dissociative adsorption of WF₆, or indirectly through reaction with HF as reaction byproduct from ligand-exchange reaction of WF₆ with Al₂O₃ starting surface. However, within the limits of characterization techniques used in this study, the type of sintering mechanism cannot be clearly discerned, as more dedicated experiments are required, including the extraction of statistically more relevant figure of merits (such as, GSD of AlF₃).

In summary, monolayer-thin WS₂ grows on amorphous Al₂O₃ by a CVD process from WF₆ and H₂S that consists out of two distinct growth regimes. During the initial growth regime, predominantly monolayer-thin WS₂ and 3D AlF₃ crystals form by a fast and self-limiting reaction with the Al₂O₃ starting surface, until the starting surface becomes completely covered (**Figure 9**). During the steady-state growth regime, a much slower reaction on the bottom, first WS₂ layer proceeds with the next WS₂ layers expanding in the lateral dimensions across the surface of the bottom, first WS₂ layer. We propose that WS₂ completely covers the Al₂O₃ starting surface during the steady-state growth regime with AlF₃ crystals residing on top of the WS₂ basal plane, which can explain why the growth almost saturates (**Figure 9**): the crystal basal plane of WS₂ is fairly unreactive towards chemisorption of WF₆^{43–45}. AlF₃ is also considered as an inert starting surface for ALD and CVD precursors due to its high stability⁴⁶. On the other hand, the WF₆ and H₂S precursors are reactive towards the Al₂O₃ surface. We therefore propose that the deposition of WS₂ almost stops when there is no more access anymore to the Al₂O₃ surface, and this is the case when the WS₂ completely covers the Al₂O₃ starting surface. The deposition is mediated by the reaction with the Al₂O₃ surface (**Figure 9**). The chemisorption of the WF₆ precursor strongly diminishes when the surface is covered with WS₂ and

AlF₃. Nonetheless, predominantly the WS₂ crystals that have formed in the second layer during the initial growth regime, continue to grow in the lateral dimensions and slowly cover the surface of the bottom, first WS₂ layer (up to 40 % after 150 minutes of deposition time). This proceeds by precursor adsorption on and diffusion across the WS₂ surface, followed by incorporation of mobile precursor species at the reactive edges of the WS₂ crystals in the second layer (**Figure 9**). The lateral growth is anticipated to proceed extremely slow due to the unreactive and self-passivating nature of the WS₂ basal plane.

FIG. 9. (color online) Model for the nucleation of WS₂ crystals during CVD process from WF₆ and H₂S on amorphous Al₂O₃ at 450 °C. Two growth regimes are distinguished based on corresponding WS₂ and AlF₃ surface coverage as indicated in Figure 6: i.e., the initial and steady-state growth regime. During the initial growth regime, the Al₂O₃ surface is readily covered with F bonded to Al, and WF₆ adsorbs locally either by dissociative or by ligand-exchange reaction. Few WS₂ nuclei start to form. (A) The amount of deposited W and S increases with deposition time, and predominantly monolayer-thin WS₂ crystals start to form albeit a second and occasional third layer can nucleate on the WS₂ basal plane already as well. Simultaneously, Al(O,F)_x surface species start to migrate on top of the growing WS₂ basal plane either by surface or gas-phase diffusion, or by a combination of both, and 3D AlF₃ crystals form. Thus, the Al₂O₃ surface mediates the nucleation of WS₂. (B) As soon as the WS₂ completely covers the Al₂O₃ surface, the amount of deposited WS₂ almost saturates. We presume the agglomerated 3D AlF₃ crystals reside on the basal plane of the bottom, first WS₂ layer. (C) During the steady-state growth regime, WS₂ crystals in the second layer grow preferentially in the lateral dimensions by precursor species that adsorb on and diffuse across the bottom, first WS₂ layer, followed by incorporation of these mobile species at the reactive edges of the crystals in the second WS₂ layer.

Few self-limiting CVD processes for WS₂ as well as other transition metal dichalcogenides including MoS₂ have been reported in literature^{47–49}. For example, Kim et al. have observed that the growth of MoS₂ from MoCl₅ and H₂S saturates when the starting surface becomes completely covered⁴⁸. In addition, they observed that the layer thickness of the deposited MoS₂ depends on the deposition temperature. Furthermore, self-limiting growth behavior is well-studied for the CVD of graphene from hydrocarbon precursors (e.g., methane (CH₄) or ethylene (C₂H₄)) and H₂ on metallic starting surfaces (e.g., Cu, Pt)^{50–52}. The metal catalyzes the growth of graphene. When the metal surface is completely covered with graphene, the precursors can no longer access the catalyst and the growth of graphene saturates. Our current study shows several similarities with self-limiting CVD growth of single layer graphene. However, the Al₂O₃ starting surface does not catalyze the growth of WS₂ but it is partially consumed by fluorination during WF₆ and H₂S exposure resulting in the formation of AlF₃ crystals. Instead, the Al₂O₃ mediates the growth of WS₂. Note the roughening that is observed underneath the AlF₃ islands in cross-sectional TEM (**Figure 7**), indicating that small amounts of Al₂O₃ are indeed consumed during CVD reaction. However the amount of consumed Al₂O₃ remains limited as no discernable decrease in the average Al₂O₃ thickness was observed by TEM or X-ray reflectivity, within the limits of detection (not shown).

In line with our results, other surface mediated reactions have been reported earlier for W CVD from the WF_6 precursor. For example, the reaction of WF_6 with other dielectric oxides, e.g., TiO_2 , and metal nitrides, e.g., TiN , was shown to result in the deposition of monolayer-thin W by direct reaction of WF_6 with TiO_2 and TiN by consuming partially the top layer of the starting surface with TiF_4 as reaction by-product⁵³. In this case, the reduction of WF_6 is enabled by reaction with the surface yielding metallic tungsten. Others reported on the controlled etching of TiO_2 by employing WF_6 as fluorinating and etching agent for atomic layer etching⁵⁴. In addition to that, W CVD from WF_6 using a Si substrate, yields metallic W by dissociative adsorption of WF_6 on Si forming volatile SiF_2 or SiF_4 ^{55,56,57}. The mechanism that we propose is in line with existing literature. It implies that the thickness of the MX_2 layer can be controlled down to a single layer provided that the CVD reaction is mediated by the starting surface, and that the adsorption reactions strongly diminish as soon as the starting surface is completely covered.

D. Functionalization of SiO_2

As it is known that the WF_6 precursor does not adsorb on the SiO_2 starting surface, we have investigated the deposition of WS_2 on functionalized SiO_2 and $\text{Al}_2\text{O}_3/\text{SiO}_2$ line patterns, to gain more insight in the CVD reaction mechanism and investigate the possibility of area-selective deposition and controlled seeding⁵⁸⁻⁶². Although the possible overall reaction equations (9-10) for WF_6 exposure to SiO_2 are thermodynamically favorable according to literature, they might be kinetically limited across the investigated CVD deposition temperature window^{58,59}.

First, we confirmed that the WF_6 precursor does not adsorb on the SiO_2 starting surface. The amount of deposited W falls below the detection limit of RBS irrespective of the WF_6 exposure times (up to 300 s) and precursor partial pressures (up to 200 mTorr) tested at 450 °C. The SiO_2 surface species are not reactive towards the WF_6 precursor, in agreement with literature on W CVD processes from WF_6 precursor^{58,63}. In line with this, no WS_2 deposition is observed for simultaneous WF_6 and H_2S exposures to the SiO_2 surface, according to AFM and RBS ($< 10^{13}$ W atoms/cm² and $< 2 \times 10^{14}$ S atoms/cm², RBS DL), and irrespective of the hydrophilicity of the SiO_2 starting surface (between $1.1 - 3.2 \times 10^{14}$ OH groups/cm² tested). Only

small amounts of organic F are detected on SiO₂ ($\leq 10^{14}$ atoms/cm²). These observations are in line with the strongly delayed growth of metallic W from WF₆ and H₂ precursors on SiO₂^{58,64}.

Interestingly, the reactivity of the SiO₂ starting surface towards the CVD precursors can be altered by exposing the surface to a single ALD reaction cycle of trimethyl aluminum (TMA) and water (H₂O). Functionalization with Al₂O₃ enables the adsorption of WF₆ on SiO₂ during the CVD process by introducing reactive surface species on the SiO₂. About $(6 \pm 1) \times 10^{13}$ W atoms/cm² adsorb during the CVD reaction, and they only partially cover the SiO₂ starting surface (~9 %) with a nucleation density of 16×10^{10} /cm² after 150 minutes of CVD reaction (**Figure 10**, AFM). The amount of deposited W is in the same order of magnitude as compared to the amount of Al adsorbed on the SiO₂ surface during the single Al₂O₃ ALD reaction cycle, which corresponds to $2 - 40 \times 10^{13}$ Al groups/cm² depending on the hydrophilicity of the starting surface. Hence, WF₆ preferentially reacts with Al-containing surface sites⁶⁵. However, the amount of deposited S falls below the detection limits of XPS and RBS, as expected for such low amounts of W deposited (DL for S, $< 2 \times 10^{14}$ S atoms/cm²). It remains noteworthy that only a small fraction of the surface is covered by WS₂, even though the functionalized SiO₂ starting surface is exposed to 150 minutes of simultaneous WF₆ and H₂S exposures. Thus, when the Al-containing surface groups are consumed, both the SiO₂ and the WS_x nuclei retain a low reactivity to WF₆ adsorption.

FIG. 10. (color online) Atomic force micrographs (1000 nm × 1000 nm) after CVD reaction of WF₆ and H₂S on a series of starting surfaces with decreasing reactivity towards the CVD precursors: 30 nm ALD Al₂O₃; thermally grown SiO₂ exposed to a single ALD reaction-cycle of Al₂O₃; and thermally grown SiO₂. The corresponding RMS surface roughness and the WS₂ crystal density (both extracted from AFM) are listed below each micrograph. The last micrograph depicts the surface roughness of the bare SiO₂ surface, for comparison. The lateral scale bars (inset, white) of the atomic force micrographs are set to 200 nm. The height scale is fixed from 0 nm to 4 nm.

When both starting surfaces are brought in close proximity by using 90 nm pitch Al₂O₃/SiO₂ line patterns, WS₂ does grow on SiO₂ and any expected selectivity to the SiO₂ surface is lost (**Figure 11a-b**). WS_x nuclei form across the SiO₂ lines, as illustrated by combining RBS, XPS and AFM. Indeed, RBS detects $(1.17 \pm 0.03) \times 10^{15}$ W atoms/cm² across the Al₂O₃/SiO₂ line patterns, which indicates that about ~30 % of the total SiO₂ surface area (including both sidewalls and top surface) is

covered with a single monolayer of WS₂, assuming that the equivalent of a single WS₂ monolayer completely covers the Al₂O₃ areas (AFM, see Figure S6, *Supplementary Material*). Furthermore, the S/W ratio across the whole line pattern is (1.6 ± 0.2) as determined from RBS, which is slightly lower compared to the S/W ratio of WS₂ on blanket Al₂O₃ of (2.0 ± 0.2) and suggests the WS₂ nuclei on the SiO₂ areas are prone to oxidation by air exposure during ex-situ RBS analysis (**Figures 1 and 4**).

In AR-XPS, the WS₂ deposition on the SiO₂ lines can be distinguished from that on the rest of the line pattern by collecting the photoelectrons at sufficiently large exit angles with respect to the normal on the sample surface (i.e., $\geq 45^\circ$ for the line pattern dimensions used in this study, see *Experimental set-up*). As such, XPS confirms that WS₂ forms on both the sidewalls and top surface of the SiO₂ lines, in addition to WS₂ deposition on Al₂O₃ (**Figure 11c**). The WS₂ doublet can be discerned from the W4f spectrum albeit metallic W and WO₃ doublets are also observed. The WO₃ likely forms from the WS_x crystal edges during air exposure as the XPS analysis is performed ex-situ, considering the small amounts of W and S deposited.

The loss in selectivity to the starting surface is also confirmed by AFM, which discerns WS_x nuclei across the SiO₂ top surface (AFM, see Figure S6, *Supplementary Material*). Also AlF₃ crystals are still observed. This selectivity loss to the starting surface can either be attributed to fluorine etch residues on the SiO₂ pattern (XPS, after CF_x plasma-based pattern etch, see Figure S7, *Supplementary Material*) which can act as reactive surface sites for precursor adsorption, or due to surface and/or gas-phase diffusion of W^{y+}F_y ($0 < y \leq 6$) species⁶⁶. In case of fluorine etch residues, AR-XPS identifies about 4.1×10^{14} F atoms/cm² on the SiO₂ lines, significantly larger compared to fluorine residues observed on non-treated SiO₂ ($< \text{DL}$, 10^{13} F atoms/cm²). For comparison, less than 10^{14} F atoms/cm² are observed when SiO₂ surface is exposed to the CVD reaction. WF₆ can chemisorb on such silicon-fluoride surface species according to reaction (11), and as such enable the nucleation of WS₂ on SiO₂. Further studies on the impact of the etch reaction chemistry are desired to isolate the role of etch residues on the adsorption behavior of the WF₆ precursor.

FIG. 11. Scanning micrographs in (a) cross-section and (b) tilted top view of patterned 50 nm $\times$ 50 nm (nominal) SiO₂ lines on 30 nm amorphous Al₂O₃ starting surface after 50 minutes of WS₂ CVD reaction (labels inset). Scale bar is 200 nm for both micrographs. (c) W4f surface spectra by AR-XPS for three different X-ray incident angles (22°, 63° and 78°) indicating the presence of WS₂ doublet ($\sim$ 33 eV), besides WO₃ ($\sim$ 36 eV). WO₃ is expected to form during ex-situ XPS analysis. For incident angles $> 45^\circ$, the SiO₂ lines predominantly contribute to the XPS intensity. In such configuration, the X-rays have to impinge perpendicular to the line pattern.

IV. CONCLUSIONS

Polycrystalline WS₂ with (0002) texture and crystal grains of up to 40 nm in lateral size and down to monolayer thickness are grown at low deposition temperature of 450 °C by the CVD reaction of WF₆ and H₂S on amorphous Al₂O₃. Besides WS₂ crystals, also AlF₃ crystals grow simultaneously. The CVD reaction is mediated by the Al₂O₃ starting surface: the precursor adsorption reaction rate strongly diminishes when the Al₂O₃ surface is no longer accessible by the precursors, as soon as the WS₂ and AlF₃ crystals completely cover the starting surface. As the WS₂ basal plane and AlF₃ have a low reactivity for

WF₆ chemisorption, the absolute amount of deposited W and S increases marginally with deposition time during the steady-state growth regime.

From analysis of the morphology of the WS₂ crystals during the CVD process, we have proposed a model for the nucleation behavior. The CVD process consists out of two growth regimes: (i) an initial growth regime that is characterized by a fast, self-limiting surface reaction with the Al₂O₃ and growth of predominantly monolayer-thin WS₂ crystals, and (ii) a steady-state growth regime that is governed by the much slower, lateral growth of WS₂ on the surface of the bottom, first WS₂ layer. During the initial growth regime, the second and third layer start to nucleate already, albeit at much lower surface coverage (< 20 %). During the steady-state growth regime, primarily WS₂ crystals in these second and occasional third layer continue to expand slowly in the lateral dimensions, while the amount of W and S on the surface increases only marginally. Presumably, these crystals grow by slow precursor adsorption on and diffusion across the WS₂ surface, followed by incorporation of mobile precursor species into the more reactive edges of the WS₂ crystals in the second layer. Crystal ripening mechanisms were not elucidated so far.

As the CVD reaction is mediated by the starting surface, accurate control over the WS₂ layer thickness as well crystal grain size might be achievable, provided that a better understanding of the underlying surface chemistry is obtained. For example, the inherent selectivity of the CVD precursors to the SiO₂ starting surface can be tuned using an Al₂O₃ functionalization layer, as the WF₆ precursor reacts preferentially with Al-containing surface groups. In that case, functionalizing the starting surface governs the reactivity of the CVD precursors to the starting surface, and can provide control over the WS₂ crystal density and grain size at low and BEOL compatible deposition temperatures. The layer thickness of the MX₂ might depend as well on the type of dielectric oxide chosen as starting surface, and opens possibilities to tailor the structural properties of the deposited MX₂.

Interestingly, functionalization of the starting surface can also provide opportunities to grow monolayer-thin MX₂ crystals at predetermined locations by selective lateral growth, in a controlled seeding approach. Such approaches intrinsically rely on the area-selective deposition from a predetermined, reactive seed⁵⁹⁻⁶¹. Hence, exploiting the observed surface selectivity of the proposed WS₂ CVD reaction in this work, can deliver the desired selectivity to fabricate monolayer-thin and (0002) textured WS₂ seeds by functionalizing the starting surface (e.g., SiO₂ starting surface with Al₂O₃) at low deposition temperatures that are compatible with a range of temperature sensitive structures (e.g., organics, BEOL structures). In addition, the occurrence of a preferential lateral growth component during the CVD reaction can tune the WS₂ crystal size, while keeping grain boundaries in the 2D material outside the active area.

SUPPLEMENTARY MATERIAL

First, the supplementary material lists the WS₂ GSDs for a discrete series of CVD deposition time (i.e., 10, 25, 50 and 150 minutes), together with the corresponding atomic force micrographs. A representative image of the crystal grain size analysis using the watershed segmentation algorithm in the *Gwyddion* analysis software is included as well (Figure S1 - S2). Furthermore, the GSD of the crystals in the second WS₂ layer evolve with the CVD deposition time (Figure S3). Also the occurrence of crystal ripening mechanisms during the CVD process is investigated by evaluating the impact of H₂S annealing (after 50 minutes of CVD reaction, Figure S4). Second, a representative Raman spectrum is included with corresponding deconvolution into the individual Raman modes using Voigt functions (Figure S5), including a tabulation of the extracted values for the difference in peak position Δk_{rel} and intensity ratio between the in-plane and out-of-plane Raman modes (Table S1 - S2). These two metrics can assess the number of layers as-deposited with CVD deposition time. Third, AFM and SEM visualize the formation of WS₂ crystals on the 90 nm pitch Al₂O₃/SiO₂ line patterns during the WS₂ CVD reaction (Figure S6). The fluorine etch residues forming on the line patterns after CF_x based plasma etch are determined using XPS (Figure S7).

ACKNOWLEDGEMENTS

The authors kindly acknowledge Johan Meersschaut, Thomas Nuytten, Thierry Conard, Danielle Vanhaeren and Christa Vrancken for RBS, Raman and PL, XPS, AFM, and SEM measurements, respectively. We are grateful for the financial support from Agency for Science and Innovation in Flanders (VLAIO, former IWT) under project no. 141640, and the imec Industrial Affiliation Beyond CMOS program.

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