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Two-Dimensional Crystal Grain Size Tuning in WS₂ Atomic Layer Deposition: an Insight in the Nucleation Mechanism

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Abstract

When two-dimensional (2D) group-VI transition metal dichalcogenides such as tungsten disulfide (WS₂) are grown by atomic layer deposition (ALD) for atomic growth control at low deposition temperatures (≤ 450 °C), they often suffer from a nanocrystalline grain structure limiting the carrier mobility. The crystallinity and monolayer thickness control during ALD of 2D materials is determined by the nucleation mechanism, which is currently not well understood. Here, we propose a qualitative model for the WS₂ nucleation behavior on dielectric surfaces during plasma-enhanced (PE-) ALD using WF₆, H₂ plasma and H₂S based on analyses of the morphology of the WS₂ crystals. The WS₂ crystal grain size increases from ~20 nm to 200 nm by lowering the nucleation density. This is achieved by lowering the precursor adsorption rate on the starting surface using an inherently less reactive starting surface, by decreasing the H₂ plasma reactivity, and by enhancing the mobility of the adsorbed species at higher

deposition temperature. Since SiO_2 is less reactive than Al_2O_3 , and diffusion and crystal ripening is enhanced at higher deposition temperature, WS_2 nucleates in an anisotropic island-like growth mode with preferential lateral growth from the WS_2 crystal edges. This work emphasizes that increasing the crystal grain size while controlling the basal plane orientation is possible during ALD at low deposition temperatures, based on insight in the nucleation behavior, which is key to advance the field of ALD of 2D materials. Moreover, this work demonstrates the conformal deposition on 3D structures, with WS_2 retaining the basal plane orientation along topographic structures.

Introduction

As dimensions in ultra-scaled nanoelectronic devices approach few-atom thickness, alternative semiconductor materials including two-dimensional (2D) transition metal dichalcogenides (MX_2 , with M a transition metal and X a chalcogen) are being researched for low-power performance devices in the back-end-of-line (BEOL)¹. It is essential to control the thickness of the 2D material at the atomic scale and to obtain high structural quality and crystallinity since this determines the semiconductor properties, and hence the electrical performance².

Ideally, the layers need to be monocrystalline as grain boundaries and intra-grain defects hinder electronic transport². Two main pathways exist that might enable the integration of highly crystalline MX_2 layers on large area substrates, i.e., the top-down and the bottom-up approach.

In the *top-down approach*, monocrystalline MX_2 is deposited by van der Waals epitaxy using a monocrystalline 2D or 3D template (e.g., graphene, sapphire). This approach delivers MX_2 layers with state-of-the-art structural and electrical properties, but requires high deposition temperatures (600 °C – 1150 °C) and epitaxial seeding³⁻⁷. Inevitably, the as-grown MX_2 requires a material transfer from that template to the target substrate. In the *bottom-up approach*, MX_2 single crystals grow by selective lateral growth at well-controlled locations on the large area substrate⁸⁻¹⁵. Understanding the reaction kinetics during the deposition process can enable the development of a selective lateral growth process of MX_2 from a pre-existing seed. The lateral dimensions of the individual crystals should align with the dimension of the device, hereby avoiding grain boundaries within the active area.

In the bottom-up approach, MX_2 layers can also be grown directly on amorphous substrates without using any template or seed, albeit the deposited layers are amorphous or polycrystalline depending on the precursors, deposition temperature and process conditions. This direct, bottom-up approach emerges as a low temperature, BEOL compatible integration route for MX_2 , provided that 2D materials can be deposited in a highly crystalline structure with a controlled number of layers and a controlled orientation of the basal planes while minimizing the density of crystal boundaries and defects. The structure and properties of the 2D layers depend on the nucleation behavior, and the deposition technique.

Today, the majority of MX₂ materials are grown by chemical vapor transport (CVT) and chemical vapor deposition (CVD) from solid phase precursors (e.g., MoO₃) and chalcogen source (e.g., S powder, H₂S) in conventional furnaces^{16–19}. By growing these materials using a dedicated precursor delivery system, the desired uniformity down to a single layer across large area substrates has been reported²⁰. In a crude approximation, the tendency in literature suggests that higher deposition temperatures (i.e., 600 °C – 1150 °C) yield highly crystalline MX₂ layers with grain sizes exceeding the micrometer range, depending on the material and precursor system. Noteworthy is that even at moderate deposition temperatures (~550 °C), grain boundaries can be minimized by carefully controlling the reaction kinetics during the CVD reaction²⁰. This holds provided that the adsorbed adatoms are sufficiently mobile to diffuse across the surface over microscopic distances and that the adsorption rate of the CVD precursors is sufficiently low.

Far less reports focus on the growth of MX₂ materials at BEOL compatible temperatures (≤ 450 °C)^{21–35}. In this context, atomic layer deposition (ALD) appeals to the scientific community: it relies on self-limiting reactions of gas-phase precursors with the surface, which occur within a specific ALD temperature window. The ALD temperature window is for most ALD processes compatible with BEOL structures. Due to the self-limiting nature of each surface reaction, atomically controlled growth is possible by ALD. Despite these advantages, only a handful of reports on MX₂ ALD have appeared in literature^{21–35}. The crystallinity and crystal grain size of the MX₂ material is limited at low deposition temperature: ALD MX₂ layers deposited at 60 °C – 450 °C are either amorphous or nanocrystalline (with lateral grain size < 100 nm).

It thus appears that, as a grim bottleneck to advance the field of ALD of MX₂, there is the lack of fundamental understanding on how the crystallinity and crystal grain size of Van der Waals bonded materials is depending on the surface chemistry and nucleation behavior during ALD. In addition, only single or few monolayers of MX₂ is desired for practical implementation. Consequently, the reaction with the starting surface becomes of the utmost importance to tailor the structure and properties of 2D layer(s). Therefore, achieving the desired structural and physical properties at low deposition temperatures relies on controlling the nucleation behavior during the ALD process.

In this work, we explore the WS₂ nucleation mechanism during plasma-enhanced (PE-) ALD based on a ternary reaction cycle –comprised of a WF₆ reaction, H₂ plasma exposure and H₂S reaction– on various dielectric surfaces. We show that the WS₂ crystal grain size can be tuned from 5 nm – 20 nm (as reported in our previous study²⁹) to beyond 200 nm by adjusting the adsorption and diffusion processes. In addition, we propose a qualitative model for the WS₂ nucleation. Lastly, we illustrate the application potential of the WS₂ PEALD layers by evaluating their semiconducting properties in a field-effect transistor using a fully BEOL compatible integration flow (FET), and by demonstrating the conformal deposition on 3D structures.

Experimental Set-up

WS₂ layers are grown by an ALD-type process where WF₆ (CAS no. 7783-82-6), H₂ plasma (CAS no. 1333-74-0) and H₂S (99.9 % pure H₂S, 10 % in He, CAS no. 7783-06-4 and 7440-59-7, respectively) are introduced into the reactor chamber sequentially, and the WS₂ film grows by means of surface reactions (Figure 1a). The precursor chemistry is chosen to pursue surface reactions that are self-limiting as verified in our earlier work, hereby minimizing gas-phase reactions²⁹. The WS₂ PEALD layers are deposited using a hot-wall, showerhead-type PECVD chamber connected to an ASM Eagle12 deposition platform. WS₂ is grown at a susceptor temperature between 300 °C and 450 °C while keeping the wall and showerhead temperature constant at 185 °C and 225 °C, respectively. One exception made to this scheme, is the growth at a susceptor temperature of 300 °C, where the wall temperature has been lowered to 175 °C instead. The ternary PEALD reaction cycle consists of a 10 s (50 sccm) WF₆ exposure, 10 s and 100 W H₂ plasma reaction, and 60 s exposure (695 sccm) to H₂S at a constant reactor chamber pressure of 2 Torr, unless reported otherwise.

The WS₂ is grown on 300 mm Si substrates covered with 30 nm amorphous ALD Al₂O₃, or 90 nm of thermally grown SiO₂. All substrates are stabilized in the PECVD reactor under N₂ for 5 minutes prior to the WS₂ deposition. The amorphous Al₂O₃ layer is grown by ALD from trimethyl aluminum (TMA, CAS no. 75-24-1) and water (H₂O) at 300 °C in a hot-wall, cross-flow type ASM Pulsar 3000 reactor. The SiO₂ is thermally grown on a Si (100) wafer in an ASM batch oven at 1000 °C in O₂ (1 atm). Water contact angles of Al₂O₃ and SiO₂ starting surfaces are (20.2 ± 0.8) ° and (39.8 ± 0.7) °, respectively, as measured

within 24 hours after deposition of the oxide layer. The water contact angles were measured using de-ionized water droplets (at room temperature) through a Dataphysics OCAH230L set-up.

To monitor how the growth of WS₂ PEALD evolves as a function of the number of PEALD reaction cycles, the amount of W and S deposited during a PEALD reaction cycle is quantified in areal density (atoms/cm²) by Rutherford backscattering spectroscopy (RBS). The compositional ratio (i.e., S/W ratio) is calculated from the measured areal densities. The chemical bonding nature and purity is measured by X-ray photoelectron spectroscopy (XPS). Furthermore, electron spin resonance (ESR) is used to reveal the defects that are created in the SiO₂ during the PEALD process. Technical details of RBS, XPS and ESR measurements are described in more detail elsewhere^{29,36,37,38}. To minimize oxidation of WS₂ layers in air during ex-situ XPS analysis, all measurements are coordinated in time after the WS₂ deposition (air exposure limited to or less than 30 minutes).

To investigate the nucleation mechanism and growth mode, atomic force microscopy (AFM) and time-of-flight secondary ion mass spectroscopy (TOFSIMS) are combined. The fractional surface coverage, crystal density and morphology (including grain size and height) of the WS₂ crystals are extracted from AFM measurements which are acquired with a Nanoscope IV instrument from ICON PT in tapping mode. The fractional WS₂ surface coverage, crystal density and grain size, are approximated by segmentation using height threshold in Gwyddion analysis software (i.e., only for non-continuous films, before layer closure)³⁹. Hereby, the grain size is defined as the diameter of the disc with equivalent projected surface area. Height of the individual crystals, i.e., the number of WS₂ layers, is determined from the corresponding height distribution profile. In order to collect statistics on the fractional surface coverage, and crystal density and grain size, four individual atomic force micrographs (of 500 nm by 500 nm) are analyzed for each deposition condition. This corresponds to up to ~ 2000 WS₂ crystals that are being analyzed for each deposition condition. Note that the WS₂ crystal density on Al₂O₃ could not be extracted using AFM as the density of crystals is too high. Therefore, it is estimated based on the total amount of deposited W by RBS after the first PEALD reaction cycle. Being sensitive to the outermost atomic layers of the surface, TOFSIMS provides essential learning about how the WS₂ covers the starting surface by analyzing the composition of the top surface^{40,41}. The WS₂ layer closure is studied by

monitoring the secondary ion surface yield of AlO_2^- and Si^+ ions for the Al_2O_3 and SiO_2 starting surface respectively, as a function of the amount of deposited W (measured by RBS), as described in more detail in our earlier work⁴².

To gain more insight into the crystalline structure of the WS_2 , as well as to visualize the nucleation of WS_2 on the closed WS_2 basal plane, the WS_2 crystals are analyzed by plan-view transmission electron microscopy (TEM) using an FEI TITAN electron microscope. The electron microscope operates at 60 kV to minimize electron beam-induced damage to the WS_2 . Therefore, the WS_2 is first transferred from the growth substrate to a holey carbon lacey TEM grid. More details on the transfer procedure are described elsewhere²⁹. Additional information about the crystallinity and texture is obtained by cross-sectional TEM using an FEI Tecnai F30 electron microscope operating at 300 kV. Furthermore, cross-sectional TEM also visualizes the conformality of the WS_2 PEALD process on 3D structures. The 3D structures consist out of ~ 90 nm high SiO_2/Si fins with an aspect ratio of approximately 4. Prior to WS_2 deposition, a 5 nm PEALD SiO_2 layer is grown on the Si fins to prevent volatile reaction of the WF_6 precursor with the Si.

To further corroborate the results on the WS_2 structural properties in TEM, both Raman spectroscopy and photoluminescence (PL) are performed using a Horiba Jobin-Yvon Labram HR Raman instrument, as described in earlier work²⁹. In addition, X-ray diffraction (XRD, Cu $K\alpha$ radiation, 50 kV, 30 mA) evaluates the crystallinity of the layers as well as how the basal plane of the WS_2 is oriented with respect to the starting surface (in Θ - 2Θ scan) and with respect to the neighboring WS_2 grains (in ω -scan). The spectra are recorded using a Bede MetrixL diffractometer from Jordan Valley.

Finally, the semiconducting properties of the WS_2 are probed by integrating the WS_2 PEALD in back-gated, and side-contacted FETs using a fully, BEOL compatible 300 mm integration flow, as described in our earlier work¹.

Results and Discussion

The paper is organized in six sections, which are outlined in a schematic representation for clarity to the reader (Figure 1b).

Figure 1. (a) Schematic of the ternary WS_2 PEALD reaction cycle, comprised of a WF_6 reaction, H_2 plasma exposure and H_2S reaction. (b) Schematic of the article outline: first, the composition, structure and crystallinity of the WS_2 PEALD layers is investigated (section 1). Since the structure and crystallinity are determined by the nucleation mechanism, the growth behavior of the WS_2 PEALD process is examined by analyzing the morphology of the WS_2 layers, including how the growth mode changes with the reactivity of the starting surface, deposition temperature, reactivity of the H_2 plasma and reactor pressure (section 2 and 3). Based on these observations, a growth model is proposed that provides insight on how the structure and crystallinity of WS_2 layers can be controlled during ALD process (section 4). The article concludes with an investigation of the growth mode during the steady-state growth regime (denoted bulk, section 5), and an exploration of the application potential of the WS_2 PEALD layers (section 6).

1. Composition and Crystal Grain Size of WS₂

In this first section, we demonstrate that WS₂ grows by PEALD on Al₂O₃ and SiO₂ and the composition (i.e., S/W ratio), crystal grain size and texture depend on the starting surface, ALD temperature and H₂ plasma reactivity.

WS₂ grows by PEALD from WF₆, H₂ plasma and H₂S between 300 °C and 450 °C on the various starting surfaces, as indicated by XPS (i.e., W4f, doublet at ~33 eV, Figure 2). The formation of WS₂ is also confirmed in the S2p surface spectra with the characteristic doublet for the W–S bond (see Figure S1 and Table S1, *Supporting Information*). Only minor contributions of WO₃ appear for WS₂ PEALD on SiO₂, except at 300 °C (between 4 % and 6 % at 350 – 450 °C, W4f doublet at ~36 eV, Figure 1). In contrast, up to ~10 % WO₃ is detected for WS₂ PEALD on Al₂O₃. The WO₃ contributions suggest that the reactive edges of the WS₂ crystals are prone to oxidation during air exposure. Since the W4f spectral peaks corresponding to WO₃ overlap with plasmon loss and W5p peaks, that WO₃ concentration is slightly overestimated.

Figure 2. Normalized W4f XPS spectra (angle-integrated) for 3-4 ML of WS₂ deposited for a series of deposition temperatures 300 °C, 350 °C, 400 °C, and 450 °C on thermally grown SiO₂, and at 300 °C on ALD Al₂O₃, respectively, and at higher reactor pressure of 8 Torr on SiO₂ (i.e., 8 Torr during the WF₆ and H₂ plasma reaction). Fixed vertical off-set is applied for clarity to the reader.

In addition, contributions of metallic tungsten W⁰ are present in the layers, mainly for WS₂ deposition on SiO₂ at low deposition temperature (at W4f doublet ~32 eV, Figure 2). The metallic contributions decrease with deposition temperature: from 17 % at 300 °C to 1 % between 350 °C – 450 °C. The W

atom needs to be reduced from the +VI (in WF_6) to the +IV oxidation state (in WS_2). Reduction and oxidation of the W atoms occurs during the H_2 plasma and H_2S reaction, respectively, and both reactions need to be carefully balanced as previously demonstrated²⁹. By increasing the deposition temperature, the reduction and oxidation are balanced which results in a well-controlled composition [S/W ratio of (1.8 ± 0.1) , XPS, and see Table S1, *Supporting Information*]. Noticeably more tungsten oxide and metallic tungsten is present for deposition at 300 °C on SiO_2 . Metallic W is not observed for WS_2 grown on Al_2O_3 , even though the deposition temperature is similar (300 °C).

Highly textured, polycrystalline WS_2 grows in a layered structure with the basal plane oriented parallel to the substrate along the [0002] crystal direction, irrespective of the starting surface, deposition temperature and reactor pressure (Figure 3a). The (0002) texture already develops at low deposition temperature of 300 °C, for about 3 ML of WS_2 , and the basal planes are only slightly tilted with respect to each other over an angle of 0.15 °. At higher deposition temperature of 450 °C, the (0002) texture strengthens, as the absolute peak intensity further increases (Figure 3a – b, and see Figure S2 *Supporting Information*). Note that some chemical vapor epitaxy processes for MoS_2 on sapphire report even lower angles of misorientation between (0002) planes of 0.01°⁴³.

Figure 3. Normalized XRD spectra for 3-4 ML of WS₂ in (a) θ - 2θ configuration (with fixed vertical off-set for clarity to the reader) and (b) ω -scan for a series of deposition temperatures between 300 °C and 450 °C on thermally grown SiO₂, and at 300 °C on ALD Al₂O₃, respectively, and at higher reactor pressure of 8 Torr on SiO₂ (i.e., 8 Torr during the WF₆ and H₂ plasma reaction); (c) 2LA(M) fwhm as a function of the W areal density (from RBS). The fwhm of the 2LA mode is extracted from the recorded Raman spectra using Voigt fitting profiles (see Figure S3, *Supporting Information*). The grey line indicates the fwhm of the 2LA mode for few-layered WS₂ by exfoliation from the natural, bulk crystal; and (d) corresponding PL response of WS₂ PEALD on amorphous ALD Al₂O₃ at 300 °C, and thermally grown SiO₂ at 300 °C and 450 °C, respectively. The PL spectrum is deconvoluted into two contributions, including the charge-neutral exciton (X⁰) and trion (X⁻) PL peak. WS₂ PEALD is grown at 2 Torr and 8 Torr (i.e., 8 Torr during the WF₆ and H₂ plasma reaction), respectively.

The maximal WS₂ crystal grain size increases from ~20 nm to 200 nm on SiO₂ by increasing the deposition temperature and reactor pressure (Figure 4). The WS₂ crystal density decreases from $(2.2 \pm 0.1) \times 10^{14}$ /cm² on Al₂O₃ to $(2.2 \pm 0.1) \times 10^{11}$ /cm² on SiO₂ by using a starting surface with an inherently lower reactivity. By increasing the deposition temperature and reactor pressure during the

PEALD reaction cycle, the crystal density on SiO₂ further decreases to $(2.4 \pm 0.2) \times 10^{10} / \text{cm}^2$, for an equivalent amount of W deposited [i.e., about $(0.60 \pm 0.02) \times 10^{15} / \text{cm}^2$]. Note that the crystal density on Al₂O₃ could not be determined from the atomic force micrographs as the individual crystals could not be clearly discerned by AFM. Therefore, the crystal density on Al₂O₃ is taken as the equivalent amount of W deposited after the first PEALD reaction cycle as determined by RBS. Likely, the crystal density is overestimated in this case, as the adsorbed species can diffuse, agglomerate and incorporate already into WS₂ clusters during the first PEALD reaction cycle, which cannot be accounted for by RBS.

Figure 4. Evolution of WS₂ crystal density and maximal crystal grain size with the reactivity of the starting surface, deposition temperature and reactor pressure. WS₂ is grown by PEALD on amorphous ALD Al₂O₃ and thermally grown SiO₂ starting surfaces at two deposition temperatures of 300 °C and 450 °C, and reactor pressures of 2 Torr and 8 Torr (i.e., 8 Torr during the WF₆ and H₂ plasma reaction), respectively. The micrographs reveal the crystalline structure of the as-grown WS₂ layers along the [0001] axis from plan-view transmission electron microscopy (300 °C, ALD Al₂O₃ and 450 °C, thermally grown SiO₂) and atomic force microscopy (only for 300 °C, thermally grown SiO₂), respectively.

Moreover, the in-plane atomic order improves at higher deposition temperature, with a stronger Raman signature and PL response as compared to the layers grown at 300 °C (Figure 3c – d, and see Figure S3 – S4, *Supporting Information*). The prominent longitudinal acoustic Raman mode 2LA(M) at the M point of the Brillouin zone, is used as fingerprint for the 2D structure of WS₂ and relates to the excitational vibration of the ensemble of S and W atoms along [0001] axis⁴⁴. The full width at half-maximum (fwhm) of the 2LA(M) mode narrows from $(20.5 \pm 0.8) \text{ cm}^{-1}$ at 300 °C on amorphous Al₂O₃ to $(13.1 \pm 0.3) \text{ cm}^{-1}$ at 450 °C on SiO₂ for similar amounts of WS₂ (Figure 3c), which appears to be in line

with the decrease in grain boundary density at higher deposition temperature. Grain boundaries distort the periodicity in the lattice and the convolution of the Raman vibrations of the neighboring grains can broaden the fwhm⁴⁵. Moreover, when increasing the reactor pressure during the PEALD reaction cycle, the fwhm of the 2LA(M) mode further decreases to $(9.7 \pm 0.2) \text{ cm}^{-1}$, approaching values reported for WS₂ flakes exfoliated from natural crystals. In addition, the WS₂ remains Raman active down a single layer, despite the low deposition temperature. The fwhm slightly decreases with the amount of WS₂ deposited on Al₂O₃(Figure 3c). This decrease in fwhm with layer thickness until bulk (>5 MLs) is in agreement with literature for both MoS₂ and WS₂⁴⁵.

The fwhm of the 2LA(M) mode for WS₂ PEALD remains only slightly larger as compared to flakes exfoliated from natural crystals [i.e., $(8.9 \pm 0.5) \text{ cm}^{-1}$], which can have several reasons. First, the synthetic WS₂ grains are randomly oriented along the [0001] crystal direction, as expected in absence of a template for epitaxial seeding. A random orientation of the crystals in the (0001) plane, and the presence of grain boundaries can broaden the 2LA(M) vibrational mode. Second, random point defects and dislocations within a single grain might contribute to fwhm line broadening as well, as shown in literature^{45,46,47}. Also, the 2D structure of the WS₂ PEALD degrades by laser irradiation during the Raman measurements as reported in our earlier work, e.g., by heating induced S loss, which might also contribute to fwhm broadening of the Raman modes²⁹.

Last, the PL response is significantly enhanced at higher deposition temperature and reactor pressure compared to the WS₂ grown at 300 °C, which confirms the improvement in the crystalline structure of the as-deposited WS₂ layers (Figure 3d, and see Figure S4, *Supporting Information*). Moreover, the fwhm narrows down to $(0.075 \pm 0.001) \text{ eV}$ for the charge-neutral exciton peak (i.e., X⁰ at 1.99 eV, a bound state of one electron and one hole), close to the values reported for exfoliated and CVD WS₂ in literature (0.04 – 0.07 eV)^{48,49}. On the other hand, a contribution from the trion PL peak (i.e., X⁻ at 1.94 eV, a bound state of two electrons and one hole) can be observed as a left-side shoulder to the X⁰ PL peak, and is a result from recombination of trions and indicates that the WS₂ PEALD is slightly doped^{49–51}. Both the assignment and positions of the PL peaks are in close agreement with recent literature reports, albeit the fwhm remains slightly larger as compared to the reported values for WS₂

flakes exfoliated from natural single crystal^{49–51}. Note that the X⁰ PL peak markedly shifts to lower energies as the deposition temperature and reactor pressure increase, which is not yet understood so far.

2. Growth Evolution of WS₂ on SiO₂ and Al₂O₃

Understanding the observed evolution in the crystallinity and crystal grain size of the WS₂ PEALD, requires an investigation of the WS₂ growth behavior across the two types of starting surfaces. This includes how the WS₂ layers start to grow on the starting surface (i.e., growth evolution) and how they cover this surface (i.e., growth mode). In this section, we compare the initial adsorption of the WF₆ precursor on two dielectric surfaces with different reactivity towards the PEALD precursors (i.e., Al₂O₃ and SiO₂), and investigate how the WS₂ continues to grow during the transition regime, until the steady-state growth regime is reached.

The nucleation of WS₂ is inhibited on SiO₂ and enhanced on Al₂O₃ starting surfaces (Figure 5). The transition regime is defined as the initial growth regime where the GPC changes as a function of the number of PEALD reaction cycles before the steady-state, linear growth regime is reached. By extrapolating the linear growth regime on SiO₂ at 300 °C, the transition regime spans ~20 PEALD reaction cycles where the nucleation of WS₂ on SiO₂ is delayed (Figure 5). The steady-state GPC is $(2.1 \pm 0.1) \times 10^{13}$ W atoms/cm²/cycle or the equivalent of ~2% of a ML per reaction cycle assuming that a fully dense and crystalline monolayer of WS₂ contains 1.16×10^{15} W atoms/cm².

Figure 5. Growth curves of WS₂ PEALD on ALD Al₂O₃ and thermally grown SiO₂ starting surfaces at 300 °C and 450 °C, respectively, and fixed reactor pressure of 2 Torr. The W areal density (as determined by RBS) is plotted as a function of the number of PEALD reaction cycles. The dotted lines are a linear fit to the data points in the steady-state growth regime. The GPC is extracted therefrom. The uncertainty on the W areal density varies up to 3%, rendering the error bars undistinguishable by eye from the data points.

The adsorption of WF₆ on the SiO₂ starting surface occurs even slower at higher deposition temperature of 450 °C, as indicated by stronger growth inhibition. Compared to 300 °C, the nucleation of WS₂ on SiO₂ is further delayed with a longer transition regime of ~75 PEALD reaction cycles (Figure 5). As the number of PEALD reaction cycles increases, the GPC increases until it eventually reaches the bulk GPC of $(3.3 \pm 0.4) \times 10^{13}$ W atoms/cm²/cycle, the equivalent of ~3 % of a ML per reaction-cycle. This increase in the GPC during the transition regime on SiO₂, confirms that while the nucleation of WS₂ on SiO₂ is initially retarded due to the lower reactivity of the starting surface, the growth from the forming WS₂ nuclei is enhanced compared to from the SiO₂ surface.

Furthermore, the SiO₂ surface becomes less reactive to the PEALD precursors at higher deposition temperatures since the span of the transition regime widens with deposition temperature. On the other hand, the formed WS₂ nuclei are more reactive towards the PEALD precursors at higher deposition temperature of 450 °C, as indicated by the slightly higher GPC as compared to 300 °C.

In contrast, the WS₂ growth is enhanced on the Al₂O₃ starting surface as compared to the bulk GPC. As reported in our earlier work, WF₆ adsorbs preferentially on the amorphous Al₂O₃ starting surface, resulting in a higher amount of deposited W of $(2.2 \pm 0.1) \times 10^{14}$ W atoms/cm² after the first PEALD reaction cycle but also large amounts of F bounded to Al ($>3 \times 10^{15}$ atoms/cm²). This substrate-enhanced growth is studied in detail in our earlier work⁴².

The delayed adsorption of the PEALD precursors on SiO₂, implies the reactivity of the native SiO₂ surface species towards the PEALD precursors is much lower compared to Al₂O₃ and that more reactive surface groups need to form during the PEALD process to enable the WF₆ adsorption. The different reactivity between SiO₂ and Al₂O₃, might stem from the difference in polarity and acidity of the native surface sites (such as hydroxyl groups) to the PEALD precursors. Indeed, the SiO₂ starting surface is less reactive towards WF₆ adsorption than Al₂O₃ during metallic W CVD and ALD at deposition temperatures between 300 °C and 450 °C, as suggested by literature reports^{52–57}. For example, the W deposition by

CVD from WF_6 and H_2 does not occur on SiO_2 substrates^{52,58}. In contrast, the nucleation of metallic W on SiO_2 is enabled by using solid Si or gas-phase Si precursors (e.g., silane SiH_4 , disilane Si_2H_6) by creating more reactive surface sites for WF_6 adsorption, such as Si-H_x ^{59,60}. During ALD of W from WF_6 and SiH_4 or Si_2H_6 , the WF_6 precursor reacts with silicon-hydrogen (Si-H) species, and fluorine ligands are removed by formation of volatile SiF_xH_y species⁶¹. Hydroxyl groups that typically terminate SiO_2 surfaces do not react with WF_6 , as adsorption of WF_6 proceeds differently compared to ALD chemistries using other metal-halide precursors (e.g., tin tetrachloride $[\text{SnCl}_4]$, aluminum trichloride $[\text{AlCl}_3]$)^{62,63}. For the latter, hydroxyl groups enable the adsorption of the metal precursor through ligand-exchange reactions.

Indeed, no growth of WS_2 occurs in a purely thermal ALD reaction cycle of WF_6 and H_2S on SiO_2 , without a H_2 plasma. The amount of W adsorbed on the SiO_2 starting surface during the initial WF_6 chemisorption reaction falls below the detection limit of RBS (DL, $< 10^{13}$ atoms/ cm^2), with only small amounts of F detected ($\leq 10^{14}$ atoms/ cm^2 , XPS). By introducing a H_2 plasma reaction in a ternary PEALD reaction cycle, the adsorption of WF_6 precursor is enabled and WS_2 can grow on SiO_2 , albeit with an initial growth delay. This suggests that the H_2 plasma modifies the nature and type of the SiO_2 surface species. That is, WF_6 adsorbs at reactive surface sites generated during the H_2 plasma reaction in the precedent PEALD reaction cycle.

However, the H_2 plasma reaction can modify the SiO_2 starting surface according to reactions (1 – 4), with the formation of both Si dangling bonds (i.e., unpaired electron denoted with $\bullet$ as in $-\text{Si}\bullet$) and/or Si-H bonds^{37,38,64,65}. Atomic hydrogen can also passivate Si dangling bonds according to reaction (3), or de-passivate silicon-hydrogen bonds (4). The equilibrium areal densities of each of the formed species will depend on the composition and conditions of the H_2 plasma. In the capacitively coupled H_2 plasma employed in this work, both hydrogen protons and atoms are present, as observed by optical emission spectroscopy (OES)²⁹.

During the H_2S reaction, the H_2S can react with the Si dangling bonds and Si-H bonds that formed during the precedent H_2 plasma reaction, either by dissociation [into $H_{(g)}$ and $SH_{(g)}$] or by ligand-exchange according to reaction pathways (5 – 6), respectively. Dissociation of the H_2S precursor at these deposition temperatures (i.e., 450°C) has been observed on a Si(100) surface⁶⁶.

During the WF_6 reaction in the next PEALD reaction cycle, WF_6 can react with both Si dangling bonds, and Si-H and Si-SH species that formed during the H_2 plasma and H_2S reaction in the precedent PEALD reaction cycle for the deposition temperature window tested and according to reaction pathway (7 – 10)⁶⁷. At a Si dangling bond, WF_6 chemisorbs through dissociative adsorption (7) or abstraction (8). This might explain why F is also detected on the SiO_2 surface ($\leq 10^{14}$ F atoms/cm², XPS). At Si-H and Si-SH surface species, WF_6 reacts by ligand-exchange (9 – 10). Note that since the WF_6 reaction precedes the H_2 plasma and H_2S reaction in the PEALD reaction cycle, we assume that WF_6 has not adsorbed on the SiO_2 starting surface after the first PEALD reaction cycle: the WF_6 precursor is not reactive towards the native SiO_2 surface species (cf., amount of deposited W and S falls below the detection limit of RBS after first PEALD reaction cycle).

Indeed, XPS identifies Si-H bonds in the SiO_2 layer after the WS_2 PEALD layers are deposited at mild H_2 plasma powers between 100 W and 400 W ($Si2p$ surface spectrum, Figure 6a – b). The Si-H bonds form in the SiO_2 layer with either three, two, one or no O atoms in the back-bonds, corresponding to Si^{3+} , Si^{2+} , Si^+ and Si^0 oxidation states at 102.3 eV, 101.4 eV, 100.5 eV and 99.5 eV, respectively^{64,65}. The $Si2p$ remains at higher binding energy of 103.6 eV corresponding to the Si^{4+} oxidation state [i.e., $Si-(O_4)$ bonding state] in bare SiO_2 layer. Peak components are assigned based on literature using pure Gaussians⁶⁸. The broadening of $Si2p$ spectra at lower binding energy is characteristic for hydrogenation

of the SiO_2 by the H_2 plasma, as described in literature⁶⁵. The relative spectral weight of the silicon suboxide components (i.e., Si^{3+} , Si^{2+} , Si^+ and Si^0 oxidation states) increases with H_2 plasma (Figure 6b). At a lower H_2 plasma power of 50 W, the $\text{Si}2\text{p}$ transition corresponds primarily to the Si^{4+} oxidation state, and Si-H bonds could not be discerned. Likely, the areal density of Si-H bonds falls below the detection limit for XPS ($<10^{14}$ atoms/ cm^2) at lower H_2 plasma powers, as the H_2 plasma does not ignite for such low plasma power. In addition, the presence of Si-S bonds cannot be completely excluded since the Si-S bonds in the $\text{Si}2\text{p}$ and $\text{S}2\text{p}$ spectra overlap with the Si-H and S-W bond, respectively.

Figure 6. (a) Normalized Si2p XPS surface spectra (angle-integrated) for the WS₂ PEALD as grown on thermally grown SiO₂ for different H₂ plasma powers (50 W, 100 W, 200 W, 400 W) at 450 °C and 2 Torr (100 PEALD reaction cycles). For clarity, only the Si2p3/2 peaks are shown in the spectrum deconvolution. Tolerable peak width and peak position broadening can vary within a 100 meV and 50 meV interval, respectively. (b) Corresponding relative spectral weight of the different components in the Si2p transition as a function of the H₂ plasma power. Each component relates to the Si atom in a different oxidation state from +IV (in SiO₂) to 0 (in Si), with the Si atom bonded to between four and none oxygen atoms in the SiO₂ network, respectively (inset); and (c) K-band ESR spectrum of 4 ML as-deposited WS₂ PEALD on thermally grown SiO₂ at 450 °C and 2 Torr (200 PEALD reaction cycles, using 100 W H₂ plasma power), and measured at 4.3 K with the applied magnetic field B_{||} [100] Si normal. Both E' defects (corresponding to O₃≡Si• centers in the SiO₂ layer) and Si/SiO₂ interface defects (P_b centers, i.e., Si₃≡Si• type defects) are detected throughout the SiO₂ layer.

Furthermore, Si dangling bond defects appear in the bulk SiO₂ after the WS₂ PEALD process with an areal density of $(3.2 \pm 0.3) \times 10^{12} / \text{cm}^2$, as quantified by ESR (Figure 6c). In the ESR spectrum, the defect-activated peak denoted as the E' contribution corresponds to a Si atom having three oxygen atoms in the back-bond and one dangling bond (i.e., unpaired electron denoted with • as in O₃≡Si•) and appears as a characteristic 'double peak' powder pattern at zero-crossing g-factor of 2.0006³⁷. These Si dangling bond defects are well-documented in literature, and typically form by displacement mechanisms such as reactive hydrogen protons and atoms that break a Si–O bond, or H detachment from existing Si–H sites in the bulk SiO₂, as described by reaction pathways (1 – 4)^{37,38}. With an unpaired electron localized at the trivalent Si center, the latter generates the E' peak in the ESR spectrum. Note that ESR cannot detect Si–H bonding centers as they are neutral in charge, as opposed to the positively charged Si dangling bonding centers.

In addition, the PEALD precursors react with adsorbed –W⁶⁺Y surface species that formed during precedent PEALD reaction cycles, as described in our earlier work^{29,42}. In view of the growth-inhibition of WS₂ on SiO₂, the adsorbed –W⁶⁺Y surface species become more reactive towards the PEALD precursors compared to the SiO₂ starting surface. The H₂ plasma can enable precursor adsorption at –W⁶⁺F_x and/or –WS_x surface species, either by removing fluorine ligands or by forming S vacancies while enabling the reduction of the W atom²⁹. Concomitantly, sufficiently long H₂S reactions are desired to achieve partial reduction of W⁶⁺ (in WF₆) to W⁴⁺ (in WS₂), and to restore S-deficient WS_x layers. Carefully balancing the H₂ plasma and H₂S reaction cumulates into a well-controllable composition of the 2D layers.

3. Growth Mode of WS₂ PEALD on Dielectrics

In section 3, we explore how the WS₂ starts to cover the starting surface during the nucleation and transition regime (i.e., the growth mode) by analyzing the fractional surface coverage, morphology and structure of WS₂ crystals using a combination of RBS, TOFSIMS, AFM and TEM. The growth mode of the WS₂ PEALD changes with the reactivity of the starting surface (3.A), the deposition temperature (3.B), the reactivity of the H₂ plasma (3.C), and the reactor pressure (3.D).

A. Reactivity of the Starting Surface

Next, we determine the growth mode of WS₂ on SiO₂ and Al₂O₃, in order to understand how the growth mode changes with the reactivity of the starting surface. By using a SiO₂ starting surface with a lower reactivity towards the PEALD precursors, the WS₂ crystal density decreases significantly compared to Al₂O₃. The density of WS₂ crystals on SiO₂ is $(2.2 \pm 0.1) \times 10^{11} / \text{cm}^2$ (AFM), which is about three orders of magnitude lower compared to the Al₂O₃ starting surface [i.e., upper limit of $(2.2 \pm 0.1) 10^{14} / \text{cm}^2$, RBS] at the same deposition temperature (300 °C, see Figure S5 – S6, *Supporting Information*, AFM). Note that the WS₂ crystal density on Al₂O₃ is most likely overestimated since it is determined by RBS from the first PEALD reaction cycle, and therefore serves only as an upper limit. After 100 PEALD reaction cycles, at least 85 % of the SiO₂ starting surface is covered with WS₂, until eventually the WS₂ completely covers the SiO₂ after 200 PEALD reaction cycles for the equivalent of ~3.3 ML (AFM, Figure 7a).

Figure 7. (a) Fractional surface coverage of WS₂ PEALD (extracted from AFM) on thermally grown SiO₂ starting surface at two deposition temperatures of 300 °C and 450 °C, and reactor pressures of 2 and 8 Torr (i.e., 8 Torr during the WF₆ and H₂ plasma reaction), respectively, as a function of the W areal density (RBS); and (b) Normalized TOFSIMS yield of secondary AlO₂⁻ and Si⁺ ions from ALD Al₂O₃ and thermally grown SiO₂ starting surface, respectively, as a function of the W areal density (RBS) and absolute monolayer content (in number of WS₂ monolayers). WS₂ PEALD is grown at 300 °C on ALD Al₂O₃ and at 300 °C and 450 °C on thermally grown SiO₂, respectively, for a constant reactor pressure of 2 Torr.

Accordingly, the WS₂ crystal grain size is larger on SiO₂ than on Al₂O₃. AFM visualizes the evolution in morphology of WS₂ on SiO₂ as a function of the number of PEALD reaction cycles (see Figure S5, *Supporting Information*). The WS₂ is nanocrystalline with a grain size varying up to 50 nm as determined from the crystal grain size distribution (GSD), and an average grain size of (21 ± 1) nm. The GSD shows the distribution of the lateral dimensions of the WS₂ crystals, after a specific number of PEALD reaction

cycles. On Al_2O_3 , the crystals are smaller, with a more narrow GSD between 5 nm and 20 nm, as studied in our earlier work⁴².

Since precursor adsorption is delayed on SiO_2 , and WF_6 preferentially adsorbs on the existing WS_2 crystals, the WS_2 grows in an island-like growth mode. TOFSIMS confirms that the WS_2 layer closure on the SiO_2 surface occurs later than on the Al_2O_3 surface (Figure 7b). The yield of the Si^+ ions from the SiO_2 underlayer decays nearly exponentially with the amount of W deposited on SiO_2 , with a fairly slow decay profile (i.e., escape depth λ of Si^+ ions from the SiO_2 underlayer, $\lambda = 0.60$) typical for island-like growth⁶⁹. Eventually, the yield of the Si^+ ions falls into the background at absolute WS_2 monolayer content of ~ 3.3 ML, which indicates that WS_2 completely covers the SiO_2 starting surface (i.e., for the equivalent of 200 PEALD reaction cycles).

In contrast, WS_2 completely covers the amorphous Al_2O_3 surface for only ~ 1.2 ML and the first WS_2 layer grows in an almost ideal layer-by-layer growth mode, with layer closure that is fast compared to conventional ALD processes (Figure 7b)⁷⁰. The decay profile of the AlO_2^+ ions from the Al_2O_3 underlayer is much steeper compared to the secondary ion yield from the SiO_2 underlayer, with a decay profile ($\lambda = 0.28$) close to that for ideal 2D or layer-by-layer growth mode⁶⁹.

B. Deposition Temperature

Despite the longer nucleation delay at 450 °C, the WS_2 completely covers the SiO_2 starting surface for an almost equivalent number of PEALD reaction cycles and amount of deposited WS_2 as compared to 300 °C (Figure 7), indicating that the WS_2 crystals grow faster in the lateral dimensions at higher deposition temperature. After 25 PEALD reaction cycles, about $(1.6 \pm 0.1) \times 10^{11}$ /cm² WS_2 crystals are deposited at higher deposition temperature of 450 °C (AFM, Figure 8a). As the number of PEALD reaction cycles increases, the amount of deposited WS_2 per reaction cycle and the fractional surface coverage increase rapidly (Figure 7a). In contrast, the crystal density decreases to $(7.5 \pm 0.6) \times 10^{10}$ /cm² after 100 PEALD reaction cycles as compared to $(22 \pm 1) \times 10^{10}$ /cm² at 300 °C [for an equivalent amount of $(0.60 \pm 0.02) \times 10^{15}$ W atoms/cm² deposited].

Figure 8. (a) Atomic force micrographs (500 nm by 500 nm) of WS₂ PEALD as a function of W areal density (RBS) on thermally grown SiO₂ at deposition temperature of 450 °C. The amount of deposited W corresponds to the following number of PEALD reaction cycles: 25, 50, 100, 150 and 200 PEALD reaction cycles (inset). (b-d) WS₂ crystal GSD for a discrete set of number of PEALD reaction cycles: 25, 50 and 100 PEALD reaction cycles. The GSDs are extracted from the corresponding atomic force micrographs, and assumed to follow a lognormal distribution as represented by the solid lines (i.e., red solid lines represent convoluted fitting profile). WS₂ PEALD is grown on thermally grown SiO₂ at 2 Torr and 450 °C. Height scale is fixed from 0 nm to 5 nm, whereas the lateral scale bar is set to 100 nm (inset) for all atomic force micrographs used in this article.

This indicates that the WS₂ crystals grow faster in the lateral dimensions at higher deposition temperature: the lateral GPC increases from (0.21 ± 0.01) nm/cycle at 300 °C to (0.44 ± 0.02) nm/cycle at 450 °C, as extracted from the GSDs. The lateral dimensions increase with the number of PEALD reaction cycles and a shoulder develops at the right-hand side of the GSD (Figure 8b-d), corresponding to the WS₂ crystals that grow in the lateral direction. The average lateral dimensions of the WS₂ crystals increase from (9 ± 5) nm at 25 PEALD reaction cycles to (44 ± 24) nm after 100 PEALD reaction cycles with a maximal crystal grain size of ~ 100 nm (Figure 8b-d).

Also, the WS₂ crystals grow preferentially in the lateral dimensions as compared to the vertical dimension: the lateral GPC of (0.44 ± 0.02) nm/cycle exceeds the vertical GPC of ~ 0.01 nm/cycle at 450 °C. The vertical GPC is extracted from the height distributions as determined by AFM (see Figure S7, *Supporting Information*). After 25 PEALD reaction cycles, monolayer-thin WS₂ crystals form (see Figure S7, *Supporting Information*). After 100 PEALD reaction cycles, the majority of the WS₂ crystals

consists already out of two monolayers, with the onset of a third layer. The preferential adsorption of the PEALD precursors on the existing WS₂ crystals prevents growth control down to a single layer. Before the WS₂ completely covers the starting surface, the height of some of the crystals can increase up to ~4–5 ML.

Hence, the WS₂ grows in an anisotropic island-like growth mode with a preferential lateral growth component. TOFSIMS confirms that the WS₂ grows in an island-like growth mode on the SiO₂ starting surface, irrespective of the deposition temperature (Figure 7b). WS₂ completely covers the SiO₂ for about similar amounts of W and S deposited at both 300 °C and 450 °C, despite the larger growth delay at higher deposition temperature.

C. H₂ Plasma Power

The WS₂ crystal density and grain size also depend on the H₂ plasma power. The crystal density of WS₂ on the SiO₂ starting surface decreases from $(28 \pm 1) \times 10^{10} / \text{cm}^2$ to $(7.5 \pm 0.6) \times 10^{10} / \text{cm}^2$ by lowering the H₂ plasma power from 400 W to 100 W, for a nearly similar amount of $(0.60 \pm 0.02) \times 10^{15}$ W atoms/cm² deposited (Figure 9a). As a result, the maximal WS₂ crystal grain size increases from 20 nm to 100 nm by decreasing the H₂ plasma power (see Figure S8, *Supporting Information*). In addition, WS₂ still grows with a well-controllable composition (S/W ratio) of (1.8 ± 0.1) (RBS, XPS) by lowering the H₂ plasma power to 100 W. The higher WS₂ crystal density with increasing H₂ plasma power, is also in line with the proposed hypothesis that the H₂ plasma reaction creates more reactive surface sites on the SiO₂, that enable the WF₆ adsorption. At the highest plasma power of 400 W tested, XPS primarily detects WO₃ indicating that the WS_x loses S. Hence, the WS_x becomes more prone to oxidation by air exposure during ex-situ XPS analysis (Figure 9b).

Figure 9. (a) WS₂ crystal density (squares, left vertical axis) and fractional surface coverage (circles, right vertical axis) of WS₂ PEALD as a function of the H₂ plasma power; and (b) Normalized W4f XPS surface spectra (angle-integrated) of WS₂ PEALD as-deposited for four different H₂ plasma powers (50 W, 100 W, 200 W, and 400 W). Fixed vertical off-set is applied for clarity to the reader. WS₂ PEALD is grown on thermally grown SiO₂ at 2 Torr and 450 °C, for 100 PEALD reaction cycles.

When the H₂ plasma power becomes too low, the amount of deposited W and S falls below the detection limit of RBS ($DL < 10^{13}$ W atoms/cm² and $< 2 \times 10^{14}$ S atoms/cm²) and the onset of WS₂ nucleation is not detected by AFM (see Figure S8, *Supporting Information*). At and below 50 W, the H₂ plasma cannot be ignited anymore. As a result, the plasma species are not sufficiently reactive to either create active surface sites on the SiO₂ for WF₆ adsorption in the next PEALD reaction cycle, or to reduce the W atom in adsorbed W⁶⁺F_x surface species, as described in our earlier work²⁹.

D. Reactor Pressure

Finally, when increasing the reactor pressure during the PEALD reaction cycle, the density of WS₂ crystals on the SiO₂ starting surface further decreases, while the adsorption of the precursors on the existing WS₂ crystals is promoted (Figure 10a, and see Figure S6, *Supporting Information*). The WS₂

crystal density can be reduced from $(7.5 \pm 0.6) \times 10^{10} / \text{cm}^2$ to $(2.4 \pm 0.2) \times 10^{10} / \text{cm}^2$ by increasing the reactor pressure to 8 Torr during the WF_6 and H_2 plasma reaction while keeping the H_2S precursor partial pressure constant (at 2 Torr reactor pressure), for an equivalent amount of deposited W [i.e., about $(0.60 \pm 0.02) \times 10^{15} \text{ W atoms/cm}^2$ deposited]. In addition, the precursor adsorption on the WS_2 crystals is strongly enhanced, which results in an increase in the lateral GPC from $(0.44 \pm 0.02) \text{ nm/cycle}$ to $(0.72 \pm 0.01) \text{ nm/cycle}$ at higher reactor pressure. When comparing the GSDs of WS_2 deposited at both reactor pressures, the average lateral dimensions of the WS_2 crystals increases further from $(44 \pm 24) \text{ nm}$ to $(72 \pm 9) \text{ nm}$ (Figure 8b-d and Figure 10b-c, respectively). The maximal crystal grain size increases up to 200 nm as compared to 100 nm at 2 Torr (TEM, Figure 10d). Both AFM and TEM discern the onset of multiple layers on the WS_2 basal plane, an effect that obviously becomes more pronounced as the number of PEALD reaction cycles increases and also leads to WS_2 spiral growth (Figure 10). Eventually, the SiO_2 starting surface gets completely covered with WS_2 after ~ 300 PEALD reaction cycles (Figure 10a).

Figure 10. (a) Atomic force micrographs (500 nm by 500 nm) of WS_2 PEALD grown at chamber pressure of 8 Torr during WF_6 and H_2 plasma reaction and 2 Torr during the H_2S reaction, as a function of the W areal density (RBS). WS_2

is deposited for 50, 100, 150 and 300 PEALD reaction cycles (inset) on thermally grown SiO₂ at 450 °C. Height scale is fixed from 0 nm to 5 nm, whereas the lateral scale bar is set to 100 nm (inset) for all atomic force micrographs used in this article. (b-c) WS₂ crystal GSD after 50 and 100 PEALD reaction cycles. The crystal grain size is approximated after analyzing the atomic force micrographs using a lognormal distribution. (d) Plan-view TEM of WS₂ grown at chamber pressure of 8 Torr during WF₆ and H₂ plasma reaction and 2 Torr during the H₂S reaction for 225 PEALD reaction cycles at 450 °C.

As described earlier, the H₂ plasma reactivity determines how the WF₆ adsorbs on the SiO₂ starting surface, which can explain the impact of reactor pressure. The type and density of reactive plasma species in capacitively coupled plasmas strongly depend on the reactor pressure which can alter the reactivity of the H₂ plasma. In a capacitively coupled plasma, the density of reactive species can diminish by increasing the reactor pressure as more gas-phase collisions between neutrals, and neutrals and excited species occur⁷¹. This results in a shorter mean free path, and the reactive species that reach the growth surface do arrive with less kinetic energy. This might at least partially explain the lower WS₂ crystal densities obtained at higher reactor pressure.

However, note that there are indications that the shape of the WS₂ crystals changes from triangular to star-like at higher H₂S partial pressure (at 8 Torr, see Figure S9, *Supporting Information*,). Clearly, the reactor pressure during the individual PEALD reactions influences the adsorption and diffusion mechanism and as such also the morphology of the growing WS₂ crystals. Hence, a more detailed study on the impact of the precursor partial pressure on the nucleation mechanism and morphology of the WS₂ crystals is desirable and subject to future research.

4. Model for the Nucleation of WS₂ on Dielectrics during PEALD

Based on these observations, we derive a qualitative model for the nucleation behavior of WS₂ on dielectric surfaces during the PEALD process. The nucleation mechanism of WS₂ encompasses following four processes: (1) precursor adsorption on both the starting surface and WS₂ crystals, (2) adatom diffusion and surface reactions, followed by (3) incorporation in existing WS₂ crystals, and (4) crystal ripening either by migration of adatoms or crystals, followed by coalescence (Figure 11)^{72,73}.

Figure 11. Schematic of the proposed qualitative model for the nucleation behavior of WS₂ PEALD, including precursor adsorption on starting surface and existing WS₂ crystals, followed by diffusion of adsorbed precursor species towards the reactive edges of the WS₂ crystals either across that starting surface or the WS₂ basal plane. The adsorbed species are incorporated in the WS₂ crystal edges. In addition, WS₂ crystals ripen either through Ostwald ripening or through coalescence of smaller WS₂ crystals. As a result of the lower reactivity of the starting surface and enhanced mobility of adatoms at higher deposition temperature, the crystal density decreases.

Lateral growth of WS₂ crystals can proceed by diffusion of W-containing species that adsorb on the SiO₂ surface or on existing WS₂ nuclei and migrate by either gas-phase or surface diffusion towards the reactive edges of the WS₂ crystals. The migrating adatoms attach at the more reactive edges of the WS₂ crystals, where incorporation in the lattice can occur. Diffusion of adsorbed species is a thermally activated process, and is therefore expected to become more pronounced at higher deposition temperature of 450 °C.

The lateral GPC during the PEALD process increases with deposition temperature at 450 °C. This can be understood from the increased reactivity of the WS₂ crystal edges and/or basal plane with deposition temperature. Indeed, the amount of deposited material will depend on the reactivity of such surface sites (i.e., of the starting surface, or the growing film) and their concentration. During an ALD process, however, also the diffusion kinetics can have an indirect impact on the GPC as it determines the morphology of the WS₂ crystals, and hereby the concentration of reactive surface sites. Because a priori self-terminating surface reactions and saturated precursor exposures are used in ALD, adsorbed precursor species will diffuse until a reactive site for chemisorption is encountered, if such reactive surface sites are not yet depleted. The reactivity of the growth surface can change for example, due to WS₂ crystal ripening or coalescence of crystals, which alters the concentration of reactive surface sites available during the PEALD process. That diffusion kinetics does play a role in how the morphology of the as grown film develops during ALD, is illustrated in this work by the WS₂ PEALD process⁷⁴.

The decrease in WS₂ crystal density on SiO₂ with the number of PEALD reaction cycles (at 450 °C), argues that crystal ripening does occur during the PEALD process either by Ostwald ripening or

Smoluchowski aggregation (i.e., dynamic coalescence)^{72,75,76}. During Ostwald ripening, WS₂ crystals are considered immobile, and larger crystals ripen at the expense of smaller crystals through atomic processes. That is, single atoms detach from the smaller crystal and diffuse either in the gas-phase or across the surface before being incorporated into the larger WS₂ crystal. During Smoluchowski aggregation, WS₂ crystals are assumed to be mobile and smaller crystals migrate across the surface until a larger aggregate forms. In this case, the morphology of the resulting WS₂ crystals will depend on how the mobility of the WS₂ crystals scales with the crystal size.

The particle size distribution (PSD) and particle spatial distribution can describe the governing growth mechanism, for a given cluster number density and surface coverage at a specific time⁷⁷. A recent, seminal work on the sintering mechanism during ALD of metal nanoparticles presented the signature for both type of ripening mechanisms by analyzing the PSDs during the ALD process, and confirmed that the PSD is indeed a “signature” of the growth mechanism^{76,78}. In case of Smoluchowski aggregation, the PSD becomes right-skewed. Concurrently, when Ostwald ripening is the dominant ripening mechanism, the PSD becomes left-skewed and narrows with increasing nanoparticle size.

Hence, one might argue that in view of the right-skewness of the GSDs for the WS₂ PEALD on SiO₂ at 450 °C (Figure 8), ripening during the PEALD process proceeds through coalescence of smaller, mobile WS₂ crystals. Furthermore, since WS₂ crystals are only van der Waals bonded to the starting surface, the surface mobility of WS₂ crystals is anticipated to be higher compared to chemisorbed species. In addition, the W–S bond is relatively strong (476.15 kJ/mol) rendering single atom detachment from WS₂ crystal (i.e., Ostwald ripening) less probable at these deposition temperatures⁷⁹. Irrespective of the type of diffusion mechanism during the PEALD process, the development of the peak on the right-hand side of the GSD illustrates that WS₂ PEALD is a diffusion-mediated process, that enables the WS₂ crystals to grow in the lateral direction by incorporating mobile adsorbed surface species at the reactive edges of the WS₂ crystals (Figure 8).

Moreover, the primary peak of the GSD remains on the left-hand side of the spectrum around ~ 10 nm crystal size, irrespective of the number of PEALD reaction cycles (Figure 8). This suggests that

continuous nucleation of smaller WS_2 crystals occurs on the starting surface as result of precursor adsorption, which takes place concomitantly with the diffusion mechanisms.

Concurrently, the next WS_2 layer nucleates on the basal plane of the WS_2 crystals presumably by direct adsorption on the basal plane. In view of the lower reactivity of the basal plane with respect to the crystal edge, the probability for lateral growth from the edge is higher compared to the onset of the next WS_2 layer.

As a result, the WS_2 grows in an anisotropic island-like growth mode during the PEALD process. Nevertheless, the WS_2 crystals are more reactive to the PEALD precursors compared to the SiO_2 starting surface, as indicated by the inhibited growth. Therefore, the next WS_2 layer starts to grow already before closure of the underlying layer has completely covered the SiO_2 starting surface, which delays layer closure.

Finally, albeit the idea to tune the morphology of the WS_2 crystals through adjusting the adsorption and diffusion kinetics in this work is similar to other CVD processes reported in literature, this is realized in a fundamentally different way for both type of deposition processes. In CVD, the reaction kinetics needs to be carefully controlled by adjusting the precursor concentrations, and by exploring the deposition temperature and reactor pressure window. In contrast, the discrete and non-continuous nature of an ALD process due to the use of saturated precursor exposures and self-limiting surface reactions, makes the growth mode in principle independent of the precursor dose (in the saturated regime) as opposed to a CVD process. Instead, control over the crystal density and grain size is obtained by minimizing the number of available reactive sites on the starting surface and the WS_2 surface, increasing the reactivity of the WS_2 crystal edges, and using sufficiently long, saturated precursor exposures to provide ample time for diffusion of active precursor species towards the crystal edges.

Moreover, lowering the reactivity of the starting surface and controlling the reactivity of H_2 plasma in the WS_2 PEALD process is one way to further diminish the nucleation density on the SiO_2 starting surface, and promote lateral growth from the WS_2 crystal edges. However, the H_2 plasma is not only required for the precursor adsorption on the SiO_2 starting surface, but also enables the partial reduction of the W atom. By adjusting the reactivity of the H_2 plasma, the crystal density can be minimized, taking

into account that the reduction of the W atom should still proceed, and the active precursor species are being incorporated pre-dominantly at the reactive crystal edges. This is achieved by either lowering the H_2 plasma power, or increasing the reactor pressure during the H_2 plasma reaction. Nonetheless, the opposite dependence of the adsorption and partial reduction reaction on the H_2 plasma reactivity, might complicate the pursuit of a window where the crystal grain size can be further increased while still depositing WS_2 with a well-controlled composition.

5. Growth Mode in the Linear Growth Regime

After the WS_2 completely covers the starting surface, the next WS_2 layers continue to grow in an anisotropic island-like growth mode on the underlying WS_2 layer, irrespective of the starting surface, deposition temperature and reactivity of the H_2 plasma (TEM, Figure 12a). Vertical growth contributions are most noticeable at higher deposition temperature (450 °C) and reactor pressure (8 Torr). The adsorption of the PEALD precursors on the underlying WS_2 layer can occur at reactive surface sites of both the WS_2 basal plane as well as WS_2 grain boundaries, by several possible pathways as described in our earlier work^{29,42}. First, the next WS_2 layer can grow by epitaxial seeding on the basal plane of the underlying WS_2 layer, which results in epitaxial alignment of that WS_2 layer with respect to the underlying WS_2 (TEM, Figure 12a). Second, when the next WS_2 layer nucleates from a grain boundary, the WS_2 layer overgrows at the boundaries of grains with different orientation resulting in loss of epitaxial alignment. Third, some WS_2 layers grow from defects in the underlying WS_2 to develop into a WS_2 spirals as well (Figure 12b). Such spiral-driven growth of WS_2 crystals is reported in literature to originate from dislocations in the underlying WS_2 ⁸⁰.

Figure 12. Plan-view transmission electron micrographs of WS₂ PEALD along [0001] axis during linear growth regime, illustrate the two different kinds of growth mechanisms for the next WS₂ layer(s) on the closed WS₂ surface: (a) epitaxial seeding of the next WS₂ layer on the underlying WS₂ crystals, and (b) spiraling growth. The WS₂ is grown for 250 PEALD reaction cycles on thermally grown SiO₂ at 450 °C and 2 Torr; and (c) GPC as a function of the deposition temperature during WS₂ PEALD process at a constant reactor pressure of 2 Torr.

Despite the anisotropic island-like growth mode, the out-of-plane orientation of the WS₂ crystals is well-controlled on amorphous starting surfaces with (0002) texture developing (Figure 3b). As the deposition temperature and reactor pressure increases, texture changes two-fold. On the one hand, the absolute peak intensity increases which suggests that the texture of a large portion of WS₂ crystals strengthens and the (0002) planes retain a slight tilt of 0.15 °. On the other hand, some crystals develop a texture with a larger angle of tilt between their (0002) planes (> 1°), as inferred by the broadening at the foot of the peak (Figure 3b). The origin of the peak broadening and tilt between the (0002) basal planes of the WS₂ crystals, could relate to how the next WS₂ layer nucleates on the underlying WS₂ layer. For example, some crystals do grow in spirals from a dislocation in the underlying WS₂ layer, and hence develop a larger tilt with respect to the neighboring grains.

Along the [0001] axis, the WS₂ is polycrystalline with a random orientation of the WS₂ crystals, as expected when the WS₂ layers either have to nucleate on an amorphous dielectric starting surface or polycrystalline WS₂ instead of a single crystalline 3D and 2D template (e.g., sapphire and monocrystalline WS₂) for epitaxial seeding.

Lastly, note that the bulk GPC at 450 °C is slightly higher compared to the GPC at 300 °C (Figure 12c). The PEALD precursors might become more reactive to the WS₂ at higher deposition temperatures which enhances the adsorption rate of WF₆ precursor on WS₂. In addition, the higher GPC might also result from the defect-induced growth contributions, such as dislocation-driven spiral growth of WS₂.

6. Application potential of WS₂ PEALD

In the last section, we illustrate the application potential of WS₂ PEALD by (i) integrating WS₂ in BEOL compatible transistors to evaluate the electronic properties, and by (ii) depositing WS₂ on 3D structures to assess the conformality.

The WS₂ shows the typical transistor response with a ratio of maximal to minimal drain current ($I_{D,max}/I_{D,min}$) of $\sim 10^5$ for 224 nm long and 1 μ m wide channels (see Figure S10a, *Supporting Information*). The WS₂ PEALD layers on SiO₂ at 450 °C and 2 Torr have been integrated into a BEOL compatible 300 mm process flow to fabricate WS₂ field-effect transistors (FETs) using a Si back gate and Mo side contacts, based on earlier work¹. WS₂ retains its characteristic 2D structure (TEM, see Figure S10b, *Supporting Information*) and the measured drain current through the WS₂ channel is fairly uniform across the 300 mm Si wafer (e.g., yield of the drain current, see Figure S11 in *Supporting Information*). Since the WS₂ does not reach saturation during the ON-state due to early gate-dielectric breakdown, mobility values cannot be extracted. Interestingly, the WS₂ PEALD transistors develop a stronger p-branch, whereas synthetic WS₂ from other ALD and CVD processes typically show n-type conductivity^{25,81,82}. The appearance of p-type conductivity in the WS₂ PEALD FETs might originate from the S-deficiency in the WS₂ layers [i.e., S/W ratio of (1.9 ± 0.1)], but this is not understood so far and warrants further investigation.

Finally, the WS₂ PEALD process provides the possibility to integrate 2D materials on 3D structures while retaining the characteristic layered structure: the WS₂ can be grown conformal on narrow fins

(with an aspect ratio of ~ 4). In most structures, the (0002) WS_2 basal planes follow the curvature of the 3D structures for few-monolayer thick WS_2 (cross-sectional TEM, Figure 13a-b). The (0002) basal planes of the WS_2 can grow along the curvature of the SiO_2 fins, both at the bottom and top of the trench, even though the precursor and H_2 plasma exposure times were not adapted to the significant increase in surface area and reduced precursor diffusion in patterned structures⁸³. In certain structures, some crystals lose the curvature of the starting surface, and stick out of the plane (Figure 13b). Ensuring that the basal planes orient parallel to the surface curvature at the bottom and top of the fins, is not trivial, as illustrated also for SnS_2 ALD⁸⁴. Furthermore, when the basal planes follow the topography of the 3D structures, the WS_2 layers develop strain which alters the bandgap of the 2D material, hereby possibly impacting the performance in a functional device. These aspects warrant further investigation.

Figure 13. Cross-sectional electron micrographs of WS_2 PEALD on Si fins coated with 5 nm PEALD grown SiO_2 (denoted hereafter as SiO_2 fins). After the WS_2 deposition (450 °C, 2 Torr), 10 nm ALD Al_2O_3 is grown on the WS_2 PEALD. (a-b) 2 – 3 ML of WS_2 PEALD with (0002) basal planes following the curvature of the fins.

Conclusions

The WS_2 PEALD proceeds by a diffusion-mediated, anisotropic island-like growth mechanism. WS_2 crystals develop by preferential lateral growth from the more reactive edges of the WS_2 crystals as opposed to the slower vertical growth by direct precursor adsorption on the basal plane. Lateral growth is enabled from the reactive WS_2 crystal edges by incorporating mobile, adsorbed surface species, hereby increasing the WS_2 crystal grain size and maintaining the (0002) texture of the basal plane at low deposition temperatures (≤ 450 °C). The WS_2 layers develop a random orientation of the crystals along [0001] crystal direction, as anticipated in absence of a template for epitaxial seeding. Moreover, the layers become optically active, yielding PL even at low deposition temperature.

Tuning the WS₂ crystal grain size at low deposition temperature intrinsically relies on lowering the precursor adsorption rate on the starting surface and enhancing diffusion of the adsorbed species in order to decrease the WS₂ crystal density on the starting surface. This is achieved in WS₂ PEALD by using a starting surface with an inherently low reactivity for WF₆ adsorption, by increasing the deposition temperature (compatible with desired temperature sensitive structures), and by lowering the reactivity of the H₂ plasma. Hence, the WS₂ crystal grain size increases up to 200 nm.

In this work, the H₂ plasma plays a dual role in enabling both the precursor adsorption on SiO₂ and the partial reduction of the W atom, which have opposite dependencies on the reactivity of the H₂ plasma. Therefore, it might prove more challenging to find such window for the WS₂ PEALD process where the crystal density can be further reduced, as long as the transition metal precursor used in the ALD process resides in a different oxidation state compared to the W atom in the final deposited film (+IV). Further increase in 2D crystal grain size should be possible by modifying the type and reactivity of the plasma used in the PEALD process. Alternative radio-frequent plasma generators or sources that sustain a plasma at lower plasma power than explored in this work, or alternative plasmas such as remote or inductively coupled, might further lower the reactivity of the plasma by eliminating the flux of reactive ions towards the surface. Hence, the precursor adsorption rate and MX₂ crystal density on the SiO₂ starting surface can be lowered further, provided that the composition of the 2D layers can be retained. Such alternatives are therefore promising approaches to consider in future work.

In that context, exploring ALD processes using alternative precursors with the transition metal atom already in the desired +IV oxidation state, will avoid the need for a partial reduction of the metal atom and might provide an even wider window where the crystal grain size can be increased even further by minimizing the nucleation density.

In conclusion, our study demonstrates how to promote lateral growth based on the insight in the nucleation behavior during the PEALD process. Such understanding of the nucleation mechanism can apply to other ALD processes of 2D materials, and provides the possibility to tailor the structure and properties of the 2D material at low deposition temperatures.

Furthermore, exploiting the predominant lateral growth component in the PEALD process might enable the growth of monocrystalline WS₂ crystals by selective lateral growth from a reactive seed in a bottom-up approach. This can be exploited to grow 2D materials at predetermined locations through area-selective deposition while keeping grain boundaries in the 2D material outside the active area. Such approach also opens opportunities for self-aligned integration schemes of 2D materials. In addition, the low deposition temperature window is compatible with a range of temperature sensitive structures (e.g., organics, BEOL structures).

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information

The following supplementary information is provided to the interested reader (in order of appearance): *Figure S1*, Normalized XPS S2p spectra (angle-integrated) for 3 – 4 ML of WS₂ on Al₂O₃ and SiO₂ at different deposition temperatures and reactor pressures, including a comparison of the composition (i.e., S/W ratio) as determined by XPS and RBS; *Figure S2*, cross-sectional electron micrographs of (0002) textured WS₂ PEALD as grown on thermally grown SiO₂ at 450 °C (2 Torr, 200 PEALD reaction cycles); *Figure S3*, normalized Raman spectra of WS₂ flake exfoliated from natural single crystal and WS₂ PEALD on Al₂O₃ and SiO₂ at different deposition temperatures and reactor pressures; *Figure S4*, repeatability of photoluminescence of WS₂ PEALD; *Figure S5*, atomic force micrographs of WS₂ PEALD

on Al₂O₃ and SiO₂ at fixed deposition temperature of 300 °C, including the GSDs for a discrete series of number of PEALD reaction cycles; *Figure S6*, crystal density of WS₂ PEALD on SiO₂ as a function of amount of deposited W at different deposition temperatures and reactor pressures; *Figure S7*, WS₂ crystal grain height distribution for a discrete series of number of PEALD reaction cycles as-deposited at 450 °C on SiO₂; *Figure S8*, atomic force micrographs of WS₂ PEALD for a series of H₂ plasma powers (50 W, 100 W, 200 W, and 400 W), as-deposited on SiO₂ at 450 °C; and *Figure S9*, atomic force micrographs of WS₂ PEALD for different precursor partial pressures on SiO₂ at 450 °C; *Figure S10* depicts the transistor response of WS₂ PEALD FETs (in back-gate configuration) for different dies across the 300 mm Si wafer and the corresponding cross-sectional electron micrograph of the WS₂ channel and Mo metal side contact device area; and, Finally *Figure S11* illustrates the corresponding yield of the drain current.

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