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Nucleation Mechanism during WS₂ Plasma Enhanced Atomic Layer Deposition on Amorphous Al₂O₃ and Sapphire Substrates

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The structure, crystallinity and properties of as-deposited two-dimensional (2D) transition metal dichalcogenides are determined by nucleation mechanisms in the deposition process. 2D materials grown by atomic layer deposition (ALD) in absence of a template, are polycrystalline or amorphous. Little is known about their nucleation mechanisms. Therefore, we investigate the nucleation behavior of WS₂ during plasma enhanced ALD from WF₆, H₂ plasma and H₂S at 300 °C on amorphous ALD Al₂O₃ starting surface and on monocrystalline, bulk sapphire. Preferential interaction of the precursors with the Al₂O₃ starting surface promotes fast closure of the WS₂ layer. The WS₂ layers are fully continuous at WS₂ content corresponding to only 1.2 WS₂ monolayers. On amorphous Al₂O₃, (0002) textured and polycrystalline WS₂ layers form with grain size of 5 nm to 20 nm due to high nucleation density ($\sim 10^{14}$ nuclei/cm²). The WS₂ growth mode changes from 2D (layer-by-layer) growth on the initial Al₂O₃ surface to three-dimensional (Volmer-Weber) growth after WS₂ layer closure. Further growth proceeds from both WS₂ basal planes in register with the underlying WS₂ grain, and from or over grain boundaries of the underlying WS₂ layer with different in-plane orientation. In contrast, on monocrystalline sapphire, WS₂ crystal grains can locally align along a preferred in-plane orientation. Epitaxial seeding occurs locally albeit a large portion of crystals remain randomly oriented, presumably due to the low deposition temperature. The WS₂ sheet resistance is 168 MΩμm suggesting that charge transport in the WS₂ layers is limited by grain boundaries.

I. INTRODUCTION

Two-dimensional transition metal dichalcogenides (2D MX_2 , with M being a transition metal and X a chalcogen) such as MoS_2 and WS_2 , are widely applicable in diverse fields ranging from nanoelectronics and –optics to catalysis and gas sensing^{1–7}. Each application requires different properties and thus structures of the 2D material, e.g., from poly- and nanocrystalline structures for catalysis to highly crystalline and monolayer (ML) thin layers with minimal defectivity in nanoelectronic devices⁸. Therefore, different manufacturable deposition techniques and integration schemes need to be developed for the different applications. For example, chemical vapor deposition (CVD) generally yields MX_2 layers with state-of-the-art semiconductor properties (i.e., high mobility), desirable in ultra-scaled nanoelectronic devices⁸. In addition, the deposition technique used to grow the 2D material also has to be compatible with the material environment. For example, only a low thermal budget is allowed for deposition on temperature sensitive structures (such as flexible organic materials)⁹. Finally, conformal deposition is required for coating nanoparticles or deposition on high aspect-ratio structures (e.g., as diffusion barrier for Cu interconnects)^{10,11}.

In this context, the development of atomic layer deposition (ALD) processes for 2D MX_2 materials gained considerable interest over recent years. The deposition principle is based on self-limiting surface reactions and enables the deposition with (sub-)ML control over large area substrates¹². In addition, due to the relatively low deposition temperature, the 2D materials can be grown directly on temperature sensitive Back-End-

Of-Line (BEOL) CMOS structures. This avoids the need for a material transfer from a growth substrate to the target substrate. Nonetheless, only few ALD processes of MoS₂ and WS₂ are reported, using dihydrogen sulfide (H₂S) in combination with either metal-halide precursors such as molybdenum pentachloride (MoCl₅) or tungsten hexafluoride (WF₆), or metal-organic precursors such as molybdenum hexacarbonyl (Mo(CO)₆), tris(2,2,6,6-tetramethylheptane-3,5-dionato) molybdenum(III) (MoThd₃) or tetrakis(dimethylamido) molybdenum Mo(NMe₂)₄^{13–17}. In the absence of a template for epitaxial seeding, the layers are either amorphous or polycrystalline, depending on the deposition temperature (typically below 450°C) and precursor chemistry.

The structure and crystallinity of ALD and CVD grown films are to a large extent determined by the nucleation and growth mechanisms. In CVD processes, the number of studies on the growth and nucleation behavior of 2D MX₂ layers has rapidly increased over the last years^{18–22}. The nucleation mechanisms determine the structure and crystal domain size. In a CVD process, the nucleation mechanisms depend on the kinetics of the surface reactions, and therefore on the precursor dose and residence time, reactor pressure and deposition temperature. For MoS₂ and WS₂ CVD from the Mo(CO)₆ and W(CO)₆ precursors respectively, a layer-by-layer growth mode is achieved by minimizing the Mo(CO)₆ and W(CO)₆ precursor dose in the presence of excess chalcogen precursor, and H₂¹⁸. Hence, the second layer starts to grow only when the first layer is completely closed. Furthermore, the nucleation density of MoS₂ on the SiO₂ starting surface is low enough ($\leq 10^{10}$ nuclei/cm²) to grow crystals with micrometer size domains.

In contrast, for 2D MX₂ ALD processes there is so far only limited understanding of the growth and nucleation mechanisms of 2D materials, and how these determine the

structure and domain size. The majority of the reports discusses the ALD process conditions and the physical properties of the grown layers^{13–17}. In general, the crystal domain size is smaller for ALD than for CVD (< 100 nm). Insight is lacking on how the ALD growth mechanisms influence the domain dimensions, the texture and the in-plane orientation of domains, and how these change during the ALD process. Such understanding is crucial to tailor the structure and properties of the layers to the requirements of a specific application.

Therefore, in this work, we investigate the nucleation mechanisms of a recently reported WS₂ PEALD process based on a ternary reaction cycle of WF₆, H₂ plasma and H₂S reactions on amorphous Al₂O₃ starting surface and on bulk, monocrystalline sapphire substrates^{23,24}. In earlier work, we have demonstrated that WS₂ layers deposited on amorphous Al₂O₃ starting surfaces have a polycrystalline structure, and the basal plane orientation depends on the deposition temperature²³. The reactions of WF₆ and H₂S are self-limiting, and the H₂ plasma reaction is essential for the deposition of WS₂ as it enables the reduction of W⁶⁺F_x surface species at low deposition temperatures (300 °C)²⁴.

The ALD growth behavior will be described by the growth-per-cycle (GPC, the amount of deposited material per reaction cycle) and the growth mode that determines how the deposited material is arranged on the substrate²⁵. The ALD growth mode can be a 2D or layer-by-layer growth, a three-dimensional (3D), Volmer-Weber or island growth, or random deposition (RD)^{26–28}. Typically, the ALD growth behavior depends on the precursors, the starting surface (the nature and density of surface species), and the deposition temperature. In addition, we will investigate the structure of the

polycrystalline WS₂ layer and the crystal domain size on the amorphous Al₂O₃ substrate, and the feasibility of epitaxial seeding using a sapphire substrate as a template.

II. EXPERIMENTAL

The WS₂ layers are deposited in a hot-wall, showerhead-type ASM PECVD reactor with direct (RF) plasma capability, connected to an Eagle12™ platform. The WS₂ is grown from a PEALD reaction cycle that consists out of a WF₆, H₂ plasma and H₂S reaction (99.9 % pure H₂S, 10 % in He) at 300 °C, with a bulk GPC of $(2.2 \pm 0.1) \times 10^{13}$ W atoms/cm² per cycle (equivalent of 0.02 ML/cycle or 0.01 nm/cycle) based on earlier work²⁴. A careful control over the H₂ plasma and H₂S reactions, results in a well-controlled composition (i.e., S/W ratio of 1.9 ± 0.1) of the layers. The H₂ plasma reaction enables the reduction of -W⁶⁺F_x surface species, but needs to be mild (100 W, 10 s) to avoid sub-surface reduction of the WS₂ layers. For detailed description of the PEALD reaction cycle and deposition conditions, the reader is referred to earlier published work^{23,24}.

The layers are grown either on 300 mm Si substrates coated with a 30 nm amorphous ALD Al₂O₃, or on monocrystalline and bulk 2 inches c-plane sapphire substrates (0001). The amorphous Al₂O₃ layer is grown by 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 the WS₂ PEALD. We investigated the PEALD WS₂ growth on pristine and annealed sapphire substrates. The pristine sapphire is annealed in a O₂:N₂ mixture (20 % of O₂) at 1050 °C for 1 hour in an ASM A400 batch oven. AFM confirms the reconstruction of the sapphire substrate (see *Supporting Information*) into atomic terraces for these annealing conditions, similar as reported elsewhere in literature²⁹.

The deposition is characterized by Rutherford backscattering spectroscopy (RBS) to quantify the areal density of W and S, and hence the composition (i.e., S/W ratio), using a 1.52 MeV He⁺ ion beam and 25 nA beam current. The incident ion beam impinges at 11° with respect to the sample normal, and the detector is placed at a scattering angle of 170°³⁰. X-ray photoelectron spectroscopy (XPS) determines the composition and chemical bonds in the deposited WS₂ layers as well as the chemical bonding nature of the starting surface. The measurements are performed using a Theta300 system from Thermo Instruments with a monochromatized Al Kα X-ray source (1486.6 eV) and a spot size of 400 μm in angle resolved (AR) mode. Binding energies are referenced to the C1s peak for all recorded spectra. After Shirley background subtraction, peaks are fitted using pseudo-Voigt functions.

The combination of time-of-flight secondary ion mass spectroscopy (TOFSIMS) and atomic force microscopy (AFM) reveals the growth mode of the WS₂ PEALD. TOFSIMS is sensitive to the outermost atomic layers of the surface, and monitors the yield of the secondary ions scattered from the sample after primary ion impact^{31,32}. For a layer-by-layer growth mode, the secondary ion surface yield of the starting surface (i.e., underlayer) decays exponentially with the amount of deposited material of the overlayer, according to

$$I = I_0 \cdot \exp\left(-\frac{x}{\lambda}\right) \quad (1)$$

with λ the escape depth of secondary ions from the underlayer and x the absolute thickness of the deposited overlayer³³. By analyzing the composition of the top surface, TOFSIMS reveals information about the layer closure of the overlayer³². A TOFSIMS IV instrument from ION-TOF GmbH is used. The WS₂ layer closure is studied by monitoring the secondary ion surface yield of AlO₂⁻ ions as a function of the amount of deposited W (measured by RBS). The surface spectra are acquired for 200 s using a 25 kV Bi³⁺ primary

ion beam (~ 0.25 pA beam current) at a 45° angle of incidence. Furthermore, the morphology of the WS_2 deposition is analyzed by AFM and the root-mean-square (RMS) roughness of the top surface is extracted. We use a Nanoscope V instrument from ICON PT (Bruker) in tapping mode.

The crystallinity of the WS_2 layer is investigated by transmission electron microscopy (TEM). Cross-sectional TEM is performed using a FEI Tecnai F30 electron microscope operating at 300 kV. For plan-view observation, the WS_2 layers are transferred from the growth substrate to a carbon lacey TEM grid, and analyzed using a FEI TITAN electron microscope operating at 60 kV to minimize the electron beam induced damage to the WS_2 ²⁴. A detailed description of the transfer procedure can be found elsewhere²⁴.

Finally, the 2D structure of the deposited layers is characterized by Raman and photoluminescence (PL) spectroscopy. A Horiba Jobin-Yvon HR800 Raman instrument is used operating with a 532 nm laser excitation wavelength at ~ 2 mW laser power and $1 \mu\text{m}^2$ laser spot size. In addition to that, a $300 \mu\text{m}$ confocal hole with a 1800 gr/mm grating is used. To limit laser induced degradation of the WS_2 layers, the laser exposure time is fixed to 200 s. The Raman spectra are corrected for the background by a blanket Si reference measurement after normalizing to the Si peak at 300 cm^{-1} . A Voight fitting profile is used to de-convolute the individual Raman modes. PL response is fitted using Gaussian profile.

Sheet resistance of the WS_2 is measured by transmission line measurements (TLM). A 4 ML WS_2 is integrated in Si back-gated and side-contacted transistors with Ti/TiN source and drain contacts and gate lengths down to 224 nm (as verified by cross-sectional TEM, not shown) on 300mm Si wafer platform³⁴. The WS_2 layers are annealed at 900°C in He prior to deposition of top 30 nm ALD Al_2O_3 (i.e., from TMA and H_2O , 300°C). More details on the transistor fabrication are reported elsewhere³⁴. Total sheet resistance is extracted at constant

source-drain voltage (V_{ds}) of 1 V from the sub-threshold regime at gate voltage (V_{gs}) of -6 V as the transistor does not reach ON-state due to gate leakage at higher values of V_{gs} . It therefore represents an upper limit to the sheet resistance.

III. RESULTS AND DISCUSSION

The paper is organized in five sections. In section 1, we describe how the WS_2 growth evolves with the number of PEALD reaction cycles on the amorphous Al_2O_3 surface at 300 °C. In section 2, we discuss the initial reaction of the precursors with the amorphous Al_2O_3 starting surface. In section 3 and 4, we monitor how the WS_2 covers the amorphous Al_2O_3 surface and continues to grow on the closed WS_2 surface, respectively. From analysis of the surface coverage, and the crystalline structure and domain size of the deposited layers (by TOFSIMS, AFM and TEM), we identify the growth mode. In section 5, we investigate how the 2D structure and orientation of WS_2 crystal domains change when growing WS_2 on monocrystalline, bulk sapphire. Finally, we evaluate the sheet resistance of the PEALD WS_2 layers by TLM.

A. ***SUBSTRATE ENHANCED GROWTH OF WS_2 PEALD ON AMORPHOUS Al_2O_3***

First, we investigate how the growth of WS_2 evolves as a function of the number of PEALD reaction cycles on amorphous ALD Al_2O_3 . In the growth curve, the amount of deposited W (areal density by RBS, detection limit of 10^{13} W atoms/cm² and 2×10^{14} S atoms/cm²) is plotted as a function of the number of PEALD reaction cycles (**Figure 1a**). Typically, three growth regimes are distinguished: a nucleation regime (1), that depends on the nature of the underlayer; the linear growth regime (3), generally

independent of the underlayer; and the transition regime (2), that denotes the transition from regime (1) to (3)²⁸. The different growth regimes are indicated in the growth curve of the PEALD WS₂ process (Figure 1a). The *bulk GPC* is denoted as the GPC during the linear growth regime, i.e., when the WS₂ grows only on the WS₂ underlayer and the Al₂O₃ starting surface is completely covered.

FIG. 1. (Color online) (a) W areal density as a function of the number of thermal ALD reaction cycles on amorphous ALD Al₂O₃ (in open, black) without H₂ plasma; and as a function of the number of PEALD reaction cycles on amorphous ALD Al₂O₃ (in closed, black) and monocrystalline, bulk sapphire (in purple) at 300 °C, respectively. The

nucleation (1), transition (2) and linear growth (3) regimes are marked to guide the eye. The dotted lines are linear fit to the data in the linear growth regime, with a bulk GPC of $(2.0 \pm 0.1) \times 10^{13}$ W atoms/cm² per cycle. The relative uncertainty on the W areal density varies between 1 % to 5 %, rendering the error bars on the graph indistinguishable by eye from the data points; and (b) S/W ratio as a function of the W areal density for the PEALD WS₂ on amorphous ALD Al₂O₃ (in black) and monocrystalline, bulk sapphire (in purple) at 300 °C, respectively.

The growth of WS₂ is enhanced by the Al₂O₃ surface, indicated by a larger GPC of WS₂ on Al₂O₃ starting surface compared to the bulk GPC. During the first PEALD reaction cycle, $(2.2 \pm 0.1) \times 10^{14}$ W atoms/cm² are deposited (Figure 1a). This amount of deposited W corresponds to 20 % of a ML of WS₂, since an ideal ML of WS₂ consists out of 1.16×10^{15} W atoms/cm². The GPC of WS₂ decreases during the transition regime (2) by about one order of magnitude.

The GPC reaches a constant value of $(2.0 \pm 0.1) \cdot 10^{13}$ W atoms/cm² or 0.01 nm/cycle after 20 PEALD reaction cycles. At that point, the total amount of deposited WS₂ is only $(1.38 \pm 0.03) \times 10^{15}$ W atoms/cm² or the equivalent of ~1.2 ML of WS₂. As a constant GPC can indicate that the Al₂O₃ surface becomes completely covered with a closed WS₂ layer, this could suggest that the layer closure of WS₂ occurs already at a WS₂ content corresponding to 1.2 ML. The fast WS₂ layer closure is verified and confirmed by TOFSIMS, as will be reported in section 3.

The bulk GPC of only ~2 % of a ML/cycle of WS₂ is low as compared to other ALD processes³⁵. As the GPC is determined by the density of reactive surface sites at the WS₂ surface, it suggests the top surface of the as-deposited WS₂ layer has a low reactivity towards the ALD precursors. The deposited WS₂ layer is polycrystalline and highly textured. Thus, the top surface consists of the WS₂ crystal basal planes and grain

boundaries. It has been observed that the crystal basal planes of 2D materials typically have a low reactivity for ALD^{36–38}. Instead, the chemisorption of ALD precursors on 2D materials can occur at line defects and grain boundaries³⁸.

Growth enhancement is not common in ALD processes²³. It has been attributed to either the topography of the starting substrate, resulting in increased surface area, and/or to an increased reactivity and/or density of reactive sites at the starting surface³⁹. As the Al₂O₃ top surface is smooth (RMS roughness = 0.15 nm, AFM) and the Al₂O₃ layer is non-porous, we conclude that the PEALD precursors are more reactive towards the Al₂O₃ surface than to the as-formed polycrystalline WS₂ layer. The WS₂ nucleation density, as estimated from the W content in the first PEALD reaction cycle, is high ($\sim 10^{14}$ /cm²).

In the linear growth regime, the S/W ratio of the WS₂ layers varies between (1.7 ± 0.1) and (2.0 ± 0.1) (**Figure 1b**, RBS). For the sub-ML coverage in the transition regime, the S/W ratio is more divergent. The following two effects can influence the variation in S/W ratio for sub-ML coverage: First, the relative uncertainty on the quantification of the amount of deposited S by RBS increases for such small amounts of deposited WS_x. Second, the layers oxidize more rapidly by the air exposure between deposition and the ex-situ RBS characterization (≤ 30 min).

B. INITIAL PRECURSOR REACTIONS ON AMORPHOUS Al₂O₃

Next, we investigate the initial reactions of the WF₆ and H₂S precursors and H₂ plasma on the amorphous Al₂O₃ surface during the first PEALD reaction cycle, in order to gain more insight in the growth enhancement that occurs during the PEALD process.

During the *WF₆ reaction*, WF₆ chemisorbs on the Al₂O₃ surface. After 1 s of WF₆ exposure, $(1.5 \pm 0.2) \times 10^{14}$ W atoms/cm² is deposited (**Figure 2a**). However, after this

initial increase in the W content, the amount of deposited W decreases exponentially for longer WF_6 exposure times. XPS shows the formation of aluminum fluoride surface species ($\sim 3 \times 10^{15}$ F atoms/cm², **Figure 2b**). This indicates that several reactions occur between WF_6 and the Al_2O_3 starting surface. WF_6 can adsorb on the Al_2O_3 surface by dissociative adsorption (I.a) or by ligand exchange reaction (I.b):

FIG. 2. (Color online) (a) W areal density as a function of the WF_6 exposure on amorphous Al_2O_3 layer at 300 °C; and (b) F1s XPS spectrum of amorphous ALD Al_2O_3 surface exposed to 60 s of WF_6 ($\sim 2.4 \times 10^6$ L) at 300 °C, indicates that F bonds to Al.

This results in the formation of both WF_{6-x} and Al–F surface species. Most likely, the W atom in the adsorbed WF_{6-x} surface species will remain in the +VI oxidation state, as no reducing agent is present and the reaction temperature is low (300 °C). The decrease in amount of deposited W for WF_6 exposures longer than 1s suggests that the as-formed $W^{6+}F_{6-x}$ surface species can desorb from the surface, presumably by the formation of volatile subfluorides (II). Alternatively, fluorination of the Al_2O_3 starting surface proceeds indirectly through reaction with HF, a reaction product of the PEALD process. The mechanism of this reaction remains to be investigated.

No growth of WS_2 occurs during sequential WF_6/H_2S reaction cycle without H_2 plasma, as evaluated by RBS (detection limit 10^{13} W atoms/cm², **Figure 1a**). In contrast, growth enhancement occurs in a PEALD reaction cycle with a H_2 plasma. During a thermal WF_6/H_2S ALD reaction cycle, the $W^{6+}F_{6-x}$ surface species remain in the +VI oxidation state as the subsequent H_2S reaction will not reduce the W^{6+} atoms as shown in earlier work²³. Hence, the tungsten fluoride desorption (reaction II) can proceed during the next ALD reaction cycles. Thus, the occurrence of reaction II can explain why no WS_2 is deposited after sequential WF_6/H_2S ALD reactions on Al_2O_3 substrates (Figure 1a). The surface gets covered by F rather than WS_2 (XPS).

In contrast, the addition of a H_2 plasma reaction in a PEALD reaction cycle enables the growth of WS_2 . The H_2 plasma reaction (III) reduces $-W^{6+}F_{6-x}$ surface species to lower oxidation states, which prevents $-W^{y+}F_{6-x}$ surface species (with $y < 6$) from desorption. The reduction of W proceeds under tested H_2 plasma conditions, as demonstrated in earlier work²³.

Thus, the combination of a 10 s WF_6 reaction with the H_2 plasma reaction prevents the chemisorbed surface species to become volatile during the next WF_6 exposure by reducing the W in the $\text{W}^{6+}\text{F}_{6-x}\text{Y}$ surface species during the H_2 plasma reaction from +VI to an intermediate oxidation state. As such, the combination of WF_6 and H_2S reaction with a H_2 plasma reaction in a PEALD reaction cycle, leads to deposition of WS_2 , which is enhanced by the Al_2O_3 surface during the nucleation and transition regime.

C. GROWTH MODE OF WS_2 PEALD ON AMORPHOUS Al_2O_3

Next, we investigate the WS_2 nucleation and growth mode on the amorphous Al_2O_3 starting surface. TOFSIMS in combination with AFM monitors the WS_2 surface coverage as a function of the amount of deposited WS_2 , from which we identify the growth mode. The preferential adsorption of the PEALD precursors on the Al_2O_3 substrate during the initial nucleation regime (1) is expected to result in a fast WS_2 layer closure. WF_6 preferentially adsorbs on the Al_2O_3 surface and/or the edges of the formed WS_2 crystals as the basal planes of these WS_2 crystals are less reactive towards chemisorption of the precursors.

Indeed, TOFSIMS shows that the WS_2 layer completely covers the surface at a WS_2 content of only 1.2 ML, the equivalent of a ~ 0.8 nm film. The yield of the AlO_2^- ions from the Al_2O_3 underlayer decays exponentially with the amount of W deposited on Al_2O_3 , with a decay profile ($\lambda = 0.28$) close to that for ideal 2D or layer-by-layer growth mode⁴⁰ (**Figure 3**). The intensity falls into the background at WS_2 content of 1.2 ML,

which indicates that WS₂ completely covers the Al₂O₃ surface. This layer closure is fast as compared to other ALD processes that behave in a growth mode that has also been described as close to 2D growth, for example HfO₂ ALD from HfCl₄ and H₂O on fully hydroxylated SiO₂ surfaces (300 °C)³³. The HfO₂ layer typically closes after $\sim 5 \times 10^{15}$ Hf atoms/cm² are deposited, which is the equivalent of a 5 ML or 1.5 nm fully dense HfO₂ film. In comparison, the WS₂ already forms a closed film for $(1.38 \pm 0.03) \times 10^{15}$ W atoms/cm², the equivalent of ~ 1.2 ML of WS₂ (~ 0.8 nm, assuming that a fully dense, crystalline ML of WS₂ consists out of 1.16×10^{15} W atoms/cm²).

FIG. 3. Normalized TOFSIMS yield of AlO₂⁻ secondary ions as a function of W areal density (RBS) and the absolute ML content (in number of MLs) for WS₂ as grown on amorphous Al₂O₃ surface. The dotted line is exponential fit to the data with $\lambda = 0.28$.

The rapid closure of the first layer of WS₂ is confirmed by plan-view TEM. WS₂ layers of only 2 ML thin can be transferred to the TEM grid for plan view TEM analysis,

and TEM confirmed that the layers are continuous films (**Figure 4a-c**). Locally some holes appear after layer transfer and they enlarge by electron beam exposure during TEM analysis (**Figure 4c**).

FIG. 4. (Color online) (a) Cross-sectional transmission micrograph of 2 ML WS₂ as grown on an amorphous 30 nm ALD Al₂O₃ underlayer; and plan-view transmission micrograph of 2 ML (b-c) and 4 ML WS₂ (d-f) as grown on 30 nm ALD Al₂O₃, illustrating the mosaic structure of the WS₂ with variation in layer thickness and with random rotation of the crystals. Locally some layers nucleate on the basal plane in register with the underlying crystal. Each color indicates a region with similar orientation and inner symmetry. (g) Corresponding fast Fourier transform (FFT) pattern of 4 ML

WS₂. The layers are grown for 65 (a-c) and 130 PEALD reaction cycles (d-g) at 300 °C, respectively.

In addition, TEM shows the structure of the WS₂ layer at atomic level, and is used to investigate the crystallinity of WS₂ layers, grain size and relative orientation of the crystal grains in the WS₂ layer. Plan view and cross-sectional TEM show that the 2 ML thin WS₂ layer is polycrystalline. The WS₂ layer is (0002) textured, with basal planes oriented parallel to the substrate (**Figure 4a**). On the other hand, the orientation of the grains along (0001) is uncontrolled as highlighted by the different colored triangles in the micrographs (**Figure 4b-c**). Each color of the highlighted triangles indicates a region with similar orientation. The corresponding fast Fourier transform (FFT) pattern confirms the individual crystals are randomly oriented along (0001) (**Figure 4g**). This is expected in absence of a template for epitaxial seeding. Note that for a WS₂ content of 2 ML, the onset of second and even third layer can be observed also from the difference in contrast (**Figure 4c**), as highlighted by the colored and marked regions.

From the corresponding dark field analysis (not shown), the crystal domain size can be extracted, and it varies between 5 nm – 20 nm. The small grain size is caused by high nucleation density ($\sim 10^{14}$ nuclei/cm²), which can be explained by the fast adsorption of the WF₆ precursor on the Al₂O₃ surface and by a low surface diffusion rate due to low deposition temperature of 300 °C. Surface diffusion is essential to enable lateral growth of ML thin 2D crystals, and micrometer grain size can be obtained at higher deposition temperatures¹⁸. Sufficient time for diffusion of the adsorbed precursor is needed, such that it can reach a reactive domain edge of the 2D crystal where lattice incorporation can occur. In the PEALD process at low temperature, the surface diffusion rate is low as

compared to the high adsorption rate of the precursors, explaining the high nucleation density and small grain size.

D. GROWTH MODE IN THE LINEAR GROWTH REGIME

Next, we investigate the growth mode of the WS₂ PEALD process after layer closure, when the WS₂ layers grow on the first closed, polycrystalline WS₂ layer. In contrast to the early nucleation regime, where the growth mode is close to 2D, we will demonstrate that after WS₂ layer closure the WS₂ growth mode becomes more 3D.

First, the RMS roughness of the WS₂ layers increases significantly with the number of PEALD reaction cycles (**Figure 5a**), which is not in line with continuation of 2D growth mode after layer closure. TEM confirms that the number of layers deposited varies locally, which becomes more pronounced for thicker layers (**Figure 4d-f**). Such difference in height of neighboring grains is apparent from the variation in contrast across the specimen with grains composed out of a different number of WS₂ layers. This confirms that the WS₂ grows in a more 3D island-like mode on the WS₂ surface due to the low reactivity of the WS₂ surface towards the PEALD precursors, in line with observations from AFM.

FIG. 5. (Color online) (a) RMS roughness of WS₂ on amorphous Al₂O₃ as determined by AFM as a function of W areal density (RBS) and absolute ML content. (b) Evolution of Raman and (c) PL response of WS₂ as a function of number of PEALD reaction cycles (as indicated in the inset). The Raman signature response of WS₂ appears after 20 PEALD reaction cycles, that is the point at which the WS₂ layer closes. Raman peak fitting (red line) and assignment based on earlier work²⁴. WS₂ is PL active after 20 PEALD reaction cycles suggesting ML coverage on Al₂O₃ starting surface. PL intensity decreases with layer thickness (i.e., number of PEALD reaction cycles), and is fitted by Gaussian (red line), with corresponding full width at half-maximum (fwhm) down to ~0.12 eV.

Second, as explained above, the bulk GPC (~ 0.01 nm/cycle) is low, confirming that the as-formed WS₂ surface has a low reactivity towards the PEALD precursors. The bulk GPC is limited by the number of reactive surface sites at the WS₂ top surface. Plan-view TEM along (0001), indicates that a next WS₂ layer grows either from the grain boundaries of the first layer or on the basal plane of the first layer. As proposed in our earlier work, -SH groups at the edges of WS₂ crystals can be reactive sites for WF₆ reaction^{24,41,42}. In addition, adsorption of WF₆ on the basal plane of WS₂ crystals cannot be excluded, e.g., at reactive sites that are created on the basal plane by H₂ plasma. In the first case, i.e., from the grain boundary, the WS₂ layer will overgrow underlying grains that are not in register with each other (**Figure 4d-f**). Moiré patterns appear as individual layers are randomly oriented on top of each other (e.g., red and blue triangle, **Figure 4e**). In the second case, i.e. for nucleation on underlying WS₂ crystal basal plane, the next layer does locally grow in register with the underlying WS₂ crystal as locally epitaxial seeding can occur (e.g., red triangles, **Figure 4c**).

Furthermore, high resolution TEM and X-ray diffraction (not shown) indicates that the WS₂ layers have the hexagonal lattice structure, with a 2H unit cell composed out of 2 single layers in a trigonal prismatic lattice coordination (**Figure 4f**).

In summary, as the WS₂ is less reactive to the PEALD precursors compared to the Al₂O₃, the WF₆ preferentially adsorbs on the Al₂O₃ surface, which leads to a high nucleation density of $\sim 10^{14}$ nuclei/cm². The combination of such high nucleation density, and pre-dominant lateral growth from the WS₂ nucleus, leads to rapid closure of WS₂ on Al₂O₃ surface for about ~ 1.2 WS₂ ML content. After layer closure, the WS₂ growth mode becomes more 3D because of the less reactive nature of the as-deposited WS₂ layer.

The WS₂ Raman signature response is observed already when the first layer of WS₂ completely covers the Al₂O₃ surface for 20 PEALD reaction cycles (**Figure 5b**). This is in agreement with TOFSIMS that indicated that layer closure occurs around 20 PEALD reaction cycles, the equivalent of ~ 1.2 ML of WS₂. Furthermore, that WS₂ layer also becomes PL active after layer closure, confirming that at least 1 ML of WS₂ is deposited across the Al₂O₃ surface (**Figure 5c**). However, the full width at half-maximum (fwhm) is large at 0.12 eV compared to exfoliated and synthesized crystals (0.04 – 0.07 eV), which suggest the WS₂ layer is fairly defective¹⁹.

Raman spectroscopy and PL qualitatively confirm that the height of the WS₂ crystals increases with the number of PEALD reaction cycles (Raman, **Figure 5b**). Indeed, the relative difference in peak position Δk_{rel} between the longitudinal acoustic and out-of-plane optical mode in Raman, i.e. the 2LA(M) and A_{1g}(Γ) respectively, increases with the number of PEALD reaction cycles (**Table 1**). This Δk_{rel} relates to the number of WS₂ monolayers, as demonstrated in literature⁴³. Thus, the Raman results

confirm that the height of the WS₂ crystals increases with the number of PEALD reaction cycles. In addition, the increase in WS₂ thickness is supported by PL: the PL intensity gradually decreases with the number of PEALD reaction cycles, due to the transition from direct to indirect bandgap when the WS₂ thickness evolves from single layer to multilayers⁴⁴.

TABLE I. Difference in peak position between 2LA(M) and E¹_{2g}(Γ), respectively, with A_{1g}(Γ) of the WS₂ Raman signature as a function of the number of PEALD reaction cycles. Error bars represent the standard deviation on the difference in peak position determined from up to four individual (unique) WS₂ depositions for each number of PEALD reaction cycles.

<i>Number of PEALD reaction cycles</i>	$\Delta k_{\text{rel}} \text{ (cm}^{-1}\text{)}$	$\Delta k_{\text{rel}} \text{ (cm}^{-1}\text{)}$
	A _{1g} – 2LA	A _{1g} – E ¹ _{2g}
20	66.4 ± 0.5	61.6 ± 0.5
65	67.7 ± 0.4	62.5 ± 0.3
130	69.8 ± 0.3	62.7 ± 1.3

E. GROWTH OF WS₂ ON MONOCRYSTALLINE SAPPHIRE SUBSTRATE

MX₂ materials are inherently bonded to the growth substrate by van der Waals forces. Such weak interactions open possibilities to grow these materials in register with a variety of monocrystalline substrates. In the case of epitaxial growth, neighboring domains have a similar crystalline orientation both in- and out-of-plane, and different domains can merge leading to a monocrystalline 2D material. Therefore, we investigate the growth of WS₂ by PEALD on the monocrystalline c-plane sapphire substrate. Several

research groups have demonstrated the epitaxial growth of 2D materials by CVD on sapphire, despite a mismatch in the lattice parameters of 34 % albeit at much higher deposition temperatures (600 °C – 1000 °C) as will be investigated here (300 °C)^{45,46}. In this section, we investigate if epitaxial seeding occurs within the ALD temperature window at deposition temperatures as low as 300 °C, and if epitaxial seeding improves by reconstructing the sapphire surface during an anneal treatment. By annealing the sapphire substrate, the surface reconstructs into a sharper terrace-and-step morphology, with the terrace width and step height determined by the anneal temperature⁴⁷.

First, we describe the growth evolution of WS₂ on pristine sapphire. The WS₂ grows fairly similar on the pristine sapphire and the amorphous Al₂O₃ starting surface. Substrate enhanced growth is observed on both surfaces. The amount of W deposited in the first PEALD reaction cycle is fairly similar, i.e. $(1.5 \pm 0.2) \times 10^{14}$ W atoms/cm² on pristine sapphire versus $(2.2 \pm 0.1) \times 10^{14}$ W atoms/cm² on amorphous Al₂O₃. The GPC decreases by almost one order of magnitude during the transition regime (2). The bulk GPC on pristine sapphire and amorphous Al₂O₃ is also comparable, i.e. $(2.4 \pm 0.1) \times 10^{13}$ W atoms/cm² per cycle on pristine sapphire versus $(2.0 \pm 0.1) \times 10^{13}$ W atoms/cm² per cycle on amorphous Al₂O₃ (**Figure 1a**). We therefore presume that the surface reaction of WF₆ as well as the growth mode of WS₂ PEALD proceed similar on the amorphous Al₂O₃ and pristine sapphire starting surface. WS₂ layer closure on sapphire will be fast due to the preferential adsorption of the precursors on the initial substrate.

The interface between the WS₂ layer and the pristine sapphire is much smoother compared to the interface with the amorphous Al₂O₃ starting surface (**Figure 4a, 6a**).

Cross-sectional TEM indicates an atomically smooth interface, as expected for a monocrystalline sapphire substrate (**Figure 6a**). Such smooth starting surface improves the crystallinity in two-fold. First, the smooth surface assists in developing a strong (0002) texture. Second, the first layer can extend more lateral to the surface due to the preferential interaction with the substrate during the nucleation and transition regime. This growth regime is characterized by 2D growth.

FIG. 6. (Color online) (a) Cross-sectional transmission micrograph of 4 ML WS₂ (i.e., nominal layer thickness for 130 PEALD reaction cycles) on monocrystalline, pristine sapphire at 300 °C, with local variation of number of layers from 4 ML to 7 ML; Plan-view scanning transmission micrograph of 2 ML – 3 ML WS₂ (i.e., nominal layer thickness for 65 PEALD reaction cycles), with local variation of number of layers up to 7 ML on (b) pristine sapphire and (c) reconstructed sapphire; (d) High resolution scanning transmission micrograph of 2 ML – 3 ML WS₂ (65 PEALD reaction cycles) on pristine sapphire, with (e) corresponding extracted intensity profile. Indicated steps in intensity profile correlate to number of individual layers in the WS₂ crystal (i.e., height).

On the other hand, the top surface remains quite rough, as indicated by the local variation in the number of layers (**Figure 6b**). This is in line with the 3D growth mode after WS₂ layer closure, similar as described above for WS₂ PEALD on amorphous Al₂O₃ surfaces. From high resolution scanning transmission electron microscopy (STEM), the WS₂ layers that nucleate on the closed WS₂ surface, grow strongly in the vertical direction with the height of these crystals correlated to the intensity profile from the scanning transmission micrograph and reaching up to 8 ML (**Figure 6d-e**).

In contrast, the morphology of the WS₂ layers changes by annealing the sapphire substrate prior to deposition: the 3D growth component present on pristine sapphire is absent on the reconstructed sapphire surface (**Figure 7**). The surface is completely covered with at least 1 ML of WS₂, with locally the onset of a second (and third) layer (**Figure 7c**). However, on pristine sapphire, at least 2 ML of WS₂ already completely cover the sapphire surface with the onset of more 3D WS₂ crystals (**Figure 7a**). This suggests that by reconstructing the sapphire substrate through annealing, the WS₂ appears to grow in a more layer-by-layer fashion, with the growth of the second layer delayed and starting only when the first layer completely covers the sapphire surface. However, note that by annealing the sapphire surface, the initial nucleation of WS₂ might be delayed with smaller amounts of WS₂ deposited on the reconstructed sapphire and thus possibly retarding the 3D growth component.

FIG. 7. Transmission electron micrographs of 2 ML – 3 ML of WS₂ (i.e., nominal layer thickness for 65 PEALD reaction cycles) grown at 300 °C on (a) pristine sapphire, and annealed sapphire at (b) 1000 °C, for 10 minutes, and (c) 1050 °C, for 60 minutes, respectively. Sapphire is annealed prior to WS₂ deposition. The low magnification images show (a) random, (b) irregular and (c) absence of 3D growth. The large patterns on the low magnification images correspond to the C-support film of the carbon lacey TEM grid on which the WS₂ is transferred.

Moreover, when the pristine sapphire substrate is annealed for much shorter annealing times of 10 minutes, the WS₂ still grows in a 3D growth mode on the closed WS₂ surface although the coverage of these 3D crystals is significantly lower compared to the pristine sapphire (**Figure 7b**). As the sapphire substrate is only partially reconstructed, nucleation of WS₂ might proceed faster compared to reconstructed sapphire, leading to the onset of 3D crystals after layer closure. Despite this apparent dependency of the morphology of the WS₂ layers on the treatment of the sapphire starting

surface, the crystal grain size of the bottom, continuous layers does not change, and remains 5 nm – 20 nm.

Next, we evaluate the in-plane orientation of the individual crystals on each sapphire starting surface by analyzing the corresponding electron diffraction patterns (see *Supporting Information*). Some of the WS₂ crystals do grow epitaxial with the sapphire, i.e., show electron diffraction intensity maxima with 60 ° in-plane symmetry as typical for the hexagonal WS₂ structure (**Figure 8**). Epitaxial seeding occurs locally, and remains faint with a comparatively wide in-plane rotation of the seeded crystals with respect to each other, as determined from the fwhm of ~20 ° – 23 ° of the intensity distribution of the <1-100> electron diffraction spots. A large part of the crystals are randomly oriented across the sapphire surface resulting in a continuous background intensity in the diffraction ring. By annealing the sapphire surface to induce surface reconstruction, the in-plane orientation of WS₂ crystals improves from a bimodal to unimodal distribution (**Figure 8**). On pristine sapphire, about half of the WS₂ grains are off-set by ~16 °. Note that such rotated crystals over 16 ° are not observed on amorphous Al₂O₃, indicating that the starting surface does influence also the crystalline structure of the as-deposited WS₂. That is, the bi- and unimodal distribution of WS₂ crystals on sapphire must stem from how the WS₂ crystals start to seed on the sapphire starting surface, and depend on how the sapphire surface is prepared.

FIG. 8. (Color online) Intensity profile along the $\langle 1-100 \rangle$ electron diffraction ring for the WS_2 layers as-deposited at 300°C on pristine and annealed sapphire (1050°C , 60 minutes). The electron diffraction patterns are acquired using a $40\ \mu\text{m}$ selected area aperture. Note that the majority of WS_2 crystal domains are randomly oriented, but through baseline correction that component is omitted from the distribution. The 60° symmetry indicates part of the crystals are grown epitaxial with the sapphire. On the pristine sapphire, about half of the WS_2 grains are off-set by $\sim 16^\circ$. WS_2 is grown at 300°C for 65 PEALD reaction cycles.

Finally, we evaluate the sheet resistance of the as-deposited 4 ML WS_2 on ALD Al_2O_3 surface (130 PEALD reaction cycles), using back-gated and side-contacted transistors on a 300 mm Si wafer platform³⁴. The WS_2 sheet resistance approaches $168\ \text{M}\Omega\mu\text{m}$, which is three orders of magnitude higher than values reported for exfoliated WS_2 flakes⁴⁸ (**Figure 9**). Note that the sheet resistance is extracted only for the sub-threshold regime, as leakage through 30 nm thin bottom Al_2O_3 prevents WS_2 channel from reaching ON-state. Hence the ON-state sheet resistance and mobility cannot be obtained, and thus the reported sheet resistance is overestimated. From subthreshold-swing (SS) of 3.5 V/dec and equivalent oxide thickness (EOT) of 15 nm, the equivalent

interface defect density (D_{it}) is calculated which approaches $8 \cdot 10^{13} / \text{cm}^2 \text{eV}$. Defects are assumed to be located at the bottom $\text{Al}_2\text{O}_3 / \text{WS}_2$ interface as well as at boundaries of crystal grains. The nanocrystalline grain structure of the WS_2 hinders charge transport, as grain boundaries act as trapping centers for the injected charge carriers. This gives rise to an increase in the layer resistance as well as high D_{it} . For applications where high mobility is required, such nanocrystalline 2D layers are not desired. For other applications, grain boundaries might be less or even not harmful. For example, in catalytic hydrogen evolution reaction (HER), the grain boundaries may acts as reactive sites due to the presence of S vacancies.

FIG. 9. Total resistance of the WS_2 (contact and channel resistance) as a function of the channel length. The dotted line is a fit to the data, from which the sheet resistance of $168 \text{ M}\Omega\mu\text{m}$ is extracted. WS_2 is grown for 130 PEALD reaction cycles at 300°C on amorphous 30 nm ALD Al_2O_3 .

IV. SUMMARY AND CONCLUSIONS

We have shown substrate enhanced growth for WS_2 PEALD on both amorphous Al_2O_3 and sapphire substrates. The precursors adsorb preferentially on the Al_2O_3 surface,

while growth on the as-formed WS₂ crystal basal planes proceeds slower. This promotes a 2D growth mode resulting in fast closure of the first WS₂ ML: the WS₂ layer is continuous and closed at WS₂ content corresponding to 1.2 ML. On the other hand, the high nucleation density of $\sim 10^{14}$ nuclei/cm² and low deposition temperature limits the crystal grain size to 5 – 20 nm. After layer closure, the WS₂ growth mode changes to more 3D growth. As a result, grains that overgrow at grain boundaries of the underlying layer develop a different in-plane orientation leading to Moiré patterns by plan-view TEM.

By revealing the nucleation mechanism, the structure and crystallinity of the deposited layers can be tailored towards specific applications. For example, in nanoelectronic devices (e.g., metal-oxide semiconductor field effect transistor), the high sheet resistance and D_{it} of the WS₂ limits charge transport, which is ultimately determined by the small WS₂ crystal grain size of 5 nm – 20 nm. The grain size is confined by the strong interaction with the starting surface that results in a high nucleation density, and limits lateral growth. However, from this insight in the nucleation mechanism, the grain size is expected to increase by reducing the nucleation density and promoting lateral growth contributions through exploring less reactive starting surfaces and deposition conditions (e.g., higher deposition temperature, less reactive H₂ plasma). This is subject of ongoing research.

Alternatively, the PEALD WS₂ layers on Al₂O₃ might be desirable for applications where grain boundaries are less or even not harmful. Since the closure and continuity of the first layer can be controlled down to 1.2 ML while retaining a (0002) orientation of the crystals at low deposition temperature, the WS₂ might become desirable

for optical applications. As ALD generally offers excellent conformality, the WS₂ layers can be used to coat catalytic nanoparticles or high aspect-ratio structures or trenches (e.g., as diffusion barriers for Cu interconnect)^{10,11}.

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TABLES

TABLE I. Difference in peak position between 2LA(M) and $E_{2g}^1(\Gamma)$, respectively, with $A_{1g}(\Gamma)$ of the WS_2 Raman signature as a function of the number of PEALD reaction cycles. Error bars represent the standard deviation on the difference in peak position determined from up to four individual (unique) WS_2 depositions for each number of PEALD reaction cycles.

<i>Number of PEALD reaction cycles</i>	$\Delta k_{rel} \text{ (cm}^{-1}\text{)}$	
	$A_{1g} - 2LA$	$A_{1g} - E_{2g}^1$
20	66.4 ± 0.5	61.6 ± 0.5
65	67.7 ± 0.4	62.5 ± 0.3
130	69.8 ± 0.3	62.7 ± 1.3

FIGURES

FIG. 1. (Color online) (a) W areal density as a function of the number of thermal ALD reaction cycles on amorphous ALD Al_2O_3 (in open, black) without H_2 plasma; and as a function of the number of PEALD reaction cycles on amorphous ALD Al_2O_3 (in closed, black) and monocrystalline, bulk sapphire (in purple) at 300 °C, respectively. The nucleation (1), transition (2) and linear growth (3) regimes are marked to guide the eye. The dotted lines are linear fit to the data in the linear growth regime, with a bulk GPC of $(2.0 \pm 0.1) \times 10^{13}$ W atoms/ cm^2 per cycle. The relative uncertainty on the W areal density varies between 1 % to 5 %, rendering the error bars on the graph indistinguishable by eye from the data points; and (b) S/W ratio as a function of the W areal density for the PEALD WS_2 on amorphous ALD Al_2O_3 (in black) and monocrystalline, bulk sapphire (in purple) at 300 °C, respectively.

FIG. 2. (Color online) (a) W areal density as a function of the WF_6 exposure on amorphous Al_2O_3 layer at 300 °C; and (b) F1s XPS spectrum of amorphous ALD Al_2O_3 surface exposed to 60 s of WF_6 ($\sim 2.4 \times 10^6$ L) at 300 °C, indicates that F bonds to Al.

FIG. 3. Normalized TOFSIMS yield of AlO_2^- secondary ions as a function of W areal density (RBS) and the absolute ML content (in number of MLs) for WS_2 as grown on amorphous Al_2O_3 surface. The dotted line is exponential fit to the data with $\lambda = 0.28$.

FIG. 4. (Color online) (a) Cross-sectional transmission micrograph of 2 ML WS_2 as grown on an amorphous 30 nm ALD Al_2O_3 underlayer; and plan-view transmission micrograph of 2 ML (b-c) and 4 ML WS_2 (d-f) as grown on 30 nm ALD Al_2O_3 , illustrating the mosaic structure of the WS_2 with variation in layer thickness and with random rotation of the crystals. Locally some layers nucleate on the basal plane in register with the underlying crystal. Each color indicates a region with similar orientation and inner symmetry. (g) Corresponding fast Fourier transform (FFT) pattern of 4 ML WS_2 . The layers are grown for 65 (a-c) and 130 PEALD reaction cycles (d-g) at 300 °C, respectively.

FIG. 5. (Color online) (a) RMS roughness of WS₂ on amorphous Al₂O₃ as determined by AFM as a function of W areal density (RBS) and absolute ML content. (b) Evolution of Raman and (c) PL response of WS₂ as a function of number of PEALD reaction cycles (as indicated in the inset). The Raman signature response of WS₂ appears after 20 PEALD reaction cycles, that is the point at which the WS₂ layer closes. Raman peak fitting (red line) and assignment based on earlier work²⁴. WS₂ is PL active after 20 PEALD reaction cycles suggesting ML coverage on Al₂O₃ starting surface. PL intensity decreases with layer thickness (i.e., number of PEALD reaction cycles), and is fitted by Gaussian (red line), with corresponding fwhm down to ~0.12 eV.

FIG. 6. (Color online) (a) Cross-sectional transmission micrograph of 4 ML WS₂ (i.e., nominal layer thickness for 130 PEALD reaction cycles) on monocrystalline, pristine sapphire at 300 °C, with local variation of number of layers from 4 ML to 7 ML; Plan-view scanning transmission micrograph of 2 ML – 3 ML WS₂ (i.e., nominal layer thickness for 65 PEALD reaction cycles), with local variation of number of layers up to 7 ML on (b) pristine sapphire and (c) reconstructed sapphire; (d) High resolution scanning transmission micrograph of 2 ML – 3 ML WS₂ (65 PEALD reaction cycles) on pristine sapphire, with (e) corresponding extracted intensity profile. Indicated steps in intensity profile correlate to number of individual layers in the WS₂ crystal (i.e., height).

FIG. 7. Transmission electron micrographs of 2 ML – 3 ML of WS₂ (i.e., nominal layer thickness for 65 PEALD reaction cycles) grown at 300 °C on (a) pristine sapphire, and annealed sapphire at (b) 1000 °C, for 10 minutes, and (c) 1050 °C, for 60 minutes, respectively. Sapphire is annealed prior to WS₂ deposition. The low magnification images show (a) random, (b) irregular and (c) absence of 3D growth. The large patterns on the low magnification images correspond to the C-support film of the carbon lacey TEM grid on which the WS₂ is transferred.

FIG. 8. (Color online) Intensity profile along the $\langle 1-100 \rangle$ electron diffraction ring for the WS_2 layers as-deposited on pristine and annealed sapphire (1050 °C, 60 minutes). The electron diffraction patterns are acquired using a 40 μm selected area aperture. Note that the majority of WS_2 crystal domains are randomly oriented, but through baseline correction that component is omitted from the distribution. The 60 ° symmetry indicates part of the crystals are grown epitaxial with the sapphire. On the pristine sapphire, about half of the WS_2 grains are off-set by $\sim 16^\circ$. WS_2 is grown at 300 °C for 65 PEALD reaction cycles.

FIG. 9. Total resistance of the WS_2 (contact and channel resistance) as a function of the channel length. The dotted line is a fit to the data, from which the sheet resistance of 168 $\text{M}\Omega\mu\text{m}$ is extracted. WS_2 is grown for 130 PEALD reaction cycles at 300 °C on amorphous 30 nm ALD Al_2O_3 .