Probing the Origin and Suppression of Vertically Oriented Nanostructures of 2D WS₂ Layers

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Supporting Information

ABSTRACT: Two-dimensional (2D) layered transition metal dichalcogenides (TMDs) such as WS₂ are promising materials for nanoelectronic applications. However, growth of the desired horizontal basal-plane oriented 2D TMD layers is often accompanied by the growth of vertical nanostructures that can hinder charge transport and, consequently, hamper device application. In this work, we discuss both the formation and suppression of vertical nanostructures during plasma-enhanced atomic layer deposition (PEALD) of WS₂. Using scanning transmission electron microscopy studies, formation pathways of vertical nanostructures are established for a two-step (AB-type) PEALD process. Grain boundaries are identified as the principal formation centers of vertical nanostructures. Based on the obtained insights, we introduce an approach to suppress the growth of vertical nanostructures wherein an additional step (C)—a chemically inert Ar plasma or a reactive H₂ plasma—is added to the original two-step (AB-type) PEALD process. This approach reduces the vertical nanostructure density by 80%. It was confirmed that suppression of vertical nanostructures goes hand in hand with grain size enhancement. The vertical nanostructure density reduction consequently lowers film resistivity by an order of magnitude.

KEYWORDS: 2D WS₂, plasma-enhanced atomic layer deposition, low-temperature processing, grain size, vertical growth of 2D layers, suppression of 2D vertical layers

INTRODUCTION

Layered, semiconducting transition metal dichalcogenides (TMDs), for example, MoS₂, WS₂, WSe₂, and so forth, are being investigated for applications in next-generation nanoelectronics, such as low-power devices in the back-end-of-line (BEOL).¹−⁴ This interest arises from their high carrier mobility, sizeable band gap, and ultrathin two-dimensional (2D) structures.¹,²−⁷ To facilitate the integration of these materials into nanoscale devices, it is crucial to synthesize high-quality crystalline TMD materials with precise thickness control to attain the desired performance levels.¹,²,³ Additionally, wafer-level scalability and conformal deposition over high-aspect-ratio three-dimensional (3D) structures at BEOL compatible temperatures (T ≤ 450 °C) are some of the other key requirements.⁸ To date, a variety of techniques have been used to synthesize monolayer to few-layer TMDs. These techniques include chemical⁹ or mechanical¹¹ exfoliation, chemical vapor deposition (CVD),¹²−¹⁵ thermal vapor sulfurization of the metal or metal oxide,¹⁶−¹⁹ physical vapor deposition (PVD),²⁰,²¹ electrochemical synthesis,²,²³ atomic layer deposition (ALD),¹,²⁴−²⁶ etc. ALD offers several benefits over other techniques because of the self-limiting nature of its gas-surface reactions.²⁶,²⁷ In essence, ALD is a cyclic thin-film deposition technique based on sequential reactions of self-limiting precursor (step A) and co-reactant (step B) exposures on the growth surface.²⁶,²⁷ Through these reactions, ALD offers the key advantages of angstrom-level thickness control, uniform film growth over large-area substrates, and conformal coatings of high-aspect-ratio 3D structures, which are otherwise difficult to achieve with other synthesis techniques.⁸,²⁷−²⁹ Typically, the deposition temperature for most ALD processes has been reported to be below 500 °C.²⁶,²⁷ In this regard, the synthesis of 2D TMDs via ALD has attracted considerable interest from the scientific community.¹⁶ Furthermore, the use of a plasma during the co-reactant exposure (step B) of an ALD cycle [the so-called plasma-enhanced ALD (PEALD) process] offers additional freedom in processing conditions that can influence material properties.²⁹−³²

To date, mono- to few-layered semiconducting TMDs, such as MoS₂,⁹,²⁴,³³−³⁸ WS₂,⁴,⁸,²⁵,³⁹,⁴⁰ WSe₂,¹¹ and so forth, have been synthesized using both thermal and PEALD on large-area substrates with precise thickness control and excellent conformality.²⁶ However, the as-deposited layers were either
amorphous or nanocrystalline with small grain sizes (<100 nm). Research on enhancing the grain sizes in ALD-deposited 2D TMDs is ongoing. Recently, Groven et al. demonstrated how the grain sizes in WS₂ films can be increased by controlling the nucleation density during ALD.

From an application perspective, another bottleneck in the progress of ALD of 2D TMDs is the growth of vertical 3D nanostructures along with the desired basal-plane-oriented (00l) 2D horizontal layers. The presence of vertical nanostructures amidst 2D layered films can lower film conductivity that hampers device performance in turn. This effect can be attributed to the anisotropic electrical conductivity of these materials. The conductivity perpendicular to the layers ([c-axis]) is approximately two orders of magnitude smaller when compared to the conductivity within the layers, that is, basal-plane-oriented (⊥c-axis). Furthermore, the vertical nanostructures can effectively scatter mobile charge carriers in these few-layered films as these nanostructures have been observed right from the film nucleation stage. Moreover, the growth of such vertical nanostructures is not restricted to TMD films synthesized using ALD alone but has been reported in the literature for TMD films obtained by CVD, thermal sulfurization of metal, sputtering, etc. In this context, suppressing the growth of vertical nanostructures in TMD films is of crucial importance for device applications. To effectively suppress the growth of vertical nanostructures, it is important to understand how they form. Understanding the formation pathways involved in the growth of vertical nanostructures can provide insights that can assist in devising methods for suppressing their growth. Although the growth of vertical nanostructures with ALD and CVD has been reported in the literature, a comprehensive formation mechanism is yet to be established. In addition, to the best of our knowledge, there are no literature reports on suppressing the vertical nanostructure growth.

In this work, we discuss both the formation and suppression of vertical nanostructures during PEALD of WS₂. Pathways involved in the formation of vertical nanostructures in a two-step (AB) WS₂ PEALD process are established based on extensive scanning transmission electron microscopy (STEM) studies. Through fast Fourier transform (FFT) analysis of atomic resolution STEM images, we demonstrate how vertical nanostructures predominantly form at grain boundaries (GBs). Furthermore, we provide insights regarding the impact of grain orientation and GB angles on the formation of vertical nanostructures. The suppression of vertical nanostructures during WS₂ PEALD was enabled through plasma-based treatments. The addition of a plasma step C to the AB process enables a significant suppression of the vertical nanostructures formed during the AB steps. We discuss how the plasma exposure in step C enables the suppression of vertical nanostructures through physical or chemical interactions as these nanostructures form and the importance of suppressing the vertical nanostructures during their nucleation. By suppressing the density of vertical nanostructures by the ABC PEALD method, we report an order of magnitude decrease in film resistivity relative to the WS₂ films deposited by an AB-only process.

**Experimental Section**

**PEALD Process.** All WS₂ depositions were performed in a commercial FlexAL ALD reactor from Oxford instruments. The reaction processes involved in the formation of vertical nanostructures during PEALD of WS₂ PEALD are established based on extensive scanning transmission electron microscopy (STEM) studies. Through fast Fourier transform (FFT) analysis of atomic resolution STEM images, we demonstrate how vertical nanostructures predominantly form at grain boundaries (GBs). Furthermore, we provide insights regarding the impact of grain orientation and GB angles on the formation of vertical nanostructures. The suppression of vertical nanostructures during WS₂ PEALD was enabled through plasma-based treatments. The addition of a plasma step C to the AB process enables a significant suppression of the vertical nanostructures formed during the AB steps. We discuss how the plasma exposure in step C enables the suppression of vertical nanostructures through physical or chemical interactions as these nanostructures form and the importance of suppressing the vertical nanostructures during their nucleation. By suppressing the density of vertical nanostructures by the ABC PEALD method, we report an order of magnitude decrease in film resistivity relative to the WS₂ films deposited by an AB-only process.
Formation of Vertical WS$_2$ Nanostructures. Formation mechanisms of vertical nanostructures have been briefly discussed in previous CVD,\textsuperscript{15,45} thermal sulfurization of metal,\textsuperscript{16,17} and ALD studies;\textsuperscript{9,38} however, a comprehensive formation mechanism has not yet been established. These formation mechanisms begin with laterally expanding grains following Frank–van der Merwe growth\textsuperscript{48} as depicted by Li et al.\textsuperscript{15} for CVD-grown MoS$_2$; all grains are considered to have their basal planes parallel to the substrate with rotational freedom around the surface normal. With an increasing number of horizontal layers, a transition from layer-by-layer growth of the TMD material to a vertical orientation (similar to Stranski–Krstanov film growth) has been reported.\textsuperscript{15} This transition was attributed to the release of strain accumulated during 2D layer growth.\textsuperscript{15,49} Such a transition has been suggested to depend on surface and growth conditions such as seed layer thickness and diffusion kinetics of vaporized chalcogen.\textsuperscript{15,50}

In the case of ALD-grown WS$_2$ films, we have suggested in our previous studies\textsuperscript{47} that the transition to vertical growth can be strongly influenced by the precursor adsorption at grain edges. Here too, the initial film growth starts with the formation of islands with basal planes oriented parallel to the substrate. The growth at the edges of these islands is faster than the growth on top of the basal planes because of the higher reactivity of edges. This aspect was well supported by DFT results, which indicated a higher precursor adsorption at the edges.\textsuperscript{47} A GB is then formed between neighboring coalescing grains (Figure 2a) during the ALD process. Precursor adsorption ensues at the WS$_2$ edges forming the GB rather than on the chemically inert basal planes, as also illustrated for the ALD of Al$_2$O$_3$ on MoS$_2$.\textsuperscript{51} Subsequent film growth occurs across the newly formed GB, resulting in the formation of vertical nanostructures. These vertical nanostructures most likely form from the culmination of several factors, including minimization of surface energy,\textsuperscript{16,52} relaxation of accumulated strain, and defect-mediated growth (at vacancies, GBs, edge/surface relocation, etc.) in as-deposited films.\textsuperscript{15,53,54} Vertical layers can also originate directly from defects present on the substrate.\textsuperscript{56} In this work, we describe three formation pathways of vertical nanostructures that were observed in PEALD WS$_2$ films: type I, type II, and type III pathways. A schematic of each formation pathway can be seen in Figure 2b–d. For these studies, WS$_2$ films deposited at 300 °C on Si substrates with 450 nm oxide using a previously established PEALD AB process were utilized.\textsuperscript{57}

The type I formation pathway (Figure 2b) arises from the continued expansion and orientation transition of one grain, while the second grain is eclipsed and expansion of the grain at this GB is terminated. This pathway begins with grain–grain interactions, resulting in preferential precursor adsorption at the edge sites of one of the two grains forming the GB. This preferential adsorption results in the continued growth of the “preferred” grain at the GB, thus blocking further precursor adsorption at the edge sites of the second grain. Further expansion of the second grain at this GB is then impracticable because of the inaccessibility of the edge sites to precursor molecules. The horizontal-to-vertical transition is fully realized as the eclipsed grain forces the continually expanding “preferred” grain to grow in a new orientation of arbitrary angle to the planes oriented parallel to the substrate. The cross-sectional STEM image in Figure 2e clearly illustrates this formation pathway with the transition site indicated by the white arrow. In this image, the WS$_2$ grain on the left is terminated by the “preferred” growth of the grain expanding from the right. Continued deposition at these newly oriented edge sites forms a vertical nanostructure. Propagation and expansion of these vertical nanostructures occur with further precursor adsorption at the now vertically oriented reactive edge sites (Figure S3). Precursor adsorption on the vertical nanostructure results in increased height and in-plane width of the vertical nanostructures. Thickening of the vertical nanostructures however follows a different adsorption pathway wherein the precursor adsorbs on a basal plane, creating a new WS$_2$ layer. This new layer can then expand conformally on the surface, resulting in vertical nanostructures with increased...
numbers of layers. Basal plane nucleation on van der Waals materials during ALD, however, is not currently a well understood phenomenon.

Next, a second type of formation was evident from our cross-sectional STEM studies involving the synergistic expansion and orientation transition of both grains forming the GB (Figure 2c). This formation contrasts with the single grain orientation transition observed in the type I pathway. We refer to this second route as the type II formation pathway. After grain coalescence, interactions between the grains forming the GB cause a transition in growth direction for both grains. This synergistic orientation transition results in the formation of vertical structures consisting of both grains.

The simultaneous transition of both grains is supported by cross-sectional STEM imaging (Figure 2f). This image clearly shows the cooperative horizontal-to-vertical transition of the coalescing grains as similarly described by Li et al. in their “Type II” growth model. Further, WS$_2$ deposition results in the propagation and expansion of the vertical nanostructure as described for the type I pathway.

Finally, we observed a third formation pathway for vertical nanostructures in PEALD WS$_2$ thin films. This pathway stands out from the other two pathways because of its seemingly disjointed, or incoherent, growth (Figure 2d). We have designated this the type III formation pathway. The two prior pathways exhibit a continuous growth of at least one of the grains forming the GB. We believe, however, that precursor adsorption can also occur on the GB, resulting in growth nearly perpendicular to the horizontally oriented basal planes, as seen in Figure 2g. The unique characteristics of this GB, however, result in the formation of a new vertically oriented WS$_2$ grain. This pathway may result from enhanced precursor adsorption at GBs that can possess a high density of defects or dislocation concentrations. Analogous to the other two pathways, vertical nanostructures formed by this pathway propagate with continued WS$_2$ deposition. However, thickening of type III vertical nanostructures results from new layer formation at, and expansion from, the GB instead of that from lateral expansion described for the previous two pathways. Precursor molecules adsorb at the edge sites of the horizontally oriented planes, yet interactions with the vertically oriented layers may lead to a continued horizontal-to-vertical orientation transition. The expanding width of the type III nanostructures may explain the observed v-shaped origin of these vertical nanostructures (Figure 2g). This phenomenon, as well as an atomistic mechanism of formation for all three formation pathways, will be investigated as part of another study. Vertical layer growth originating directly on the substrate was not observed in Figure 2. Such features grown by this pathway may be eliminated during PEALD processing, as their presence was not confirmed in this study.

We show in the above depictions that the vertical nanostructures form at GBs (Figure 2). To corroborate this, we utilized top-view high-resolution HAADF-STEM imaging, as shown in Figure 3a. We studied grain orientations on opposing sides of several vertical nanostructures in 2 nm thick WS$_2$ films. The vertical nanostructures are recognizable in STEM imaging not only from the increased contrast but also by the larger spacing between the (001) lattice planes. A vertical nanostructure is presented in Figure 3a with four color-coded areas, indicating the regions where FFTs were obtained. The FFTs of selected areas in the STEM images were utilized to establish the local in-plane grain orientation by measuring the in-plane position of crystallographically equivalent (010) spots. In Figure 3b–e, representative (010) spots are indicated by circles. These measurements reveal very similar in-plane orientations of the red, green, and blue areas; however, there is a misorientation of $\sim 7^\circ$ between these three areas and the yellow area. This misorientation angle indicates a difference in grain orientation, implying the presence of a new grain at this location. Additional measurements around several vertical nanostructures presented similar results, as will be shown below, supporting the hypothesis that vertical nanostructures originate at GBs.

Next, grain orientation studies were carried out in regions around GBs lacking vertical nanostructures. An interesting trend arises when comparing misorientation angles of GBs with and without vertical nanostructures: vertical nanostructures predominantly form at GBs with low misorientation angles (low-angle GBs). Around vertical nanostructures, the average misorientation angle was $\sim 5.6^\circ$, whereas GBs lacking a vertical nanostructure had an average misorientation angle of $\sim 16.4^\circ$. 

![Figure 3. (a) High-resolution top-view HAADF-STEM image of a vertical nanostructure in a PEALD WS$_2$ film. The four squares (red, yellow, green, and blue) correspond to the similarly outlined FFTs (b–e). The circles and numbers indicate crystallographically equivalent spots and the angle of the selected spot relative to the horizontal, respectively.](image-url)
The measured misorientation angles at GBs with and without vertical nanostructures are shown in Figure 4. It is worth noting that grain misorientation angles above 30° are indistinguishable from those below 30° because of the hexagonal symmetry of WS2, as demonstrated by the hexagonal pattern in the FFTs (Figure 3b–e). Thus, all misorientation angles are reported as 30° or less. Thicker 6 nm WS2 films deposited by the same process yielded analogous misorientation angles at GBs with and without vertical nanostructures. We believe that this predisposition to form at low misorientation angles can be partially attributed to the defect concentration and strain associated at GBs. Azizi et al. showed that higher misorientation angles result in higher local strain and dislocation concentrations at GBs. However, these two attributes also result in a higher dislocation mobility. Higher mobility of edge defects/dislocations could significantly affect precursor adsorption and edge stability, thereby decreasing the likelihood of vertical nanostructure formation at higher misorientation angles.

**Suppression of Vertical WS2 Nanostructures.** The presence of vertical nanostructures in 2D thin films such as WS2 can hinder charge transport and, consequently, hamper device performance. Conceivably, there are methods by which the formation of these undesired nanostructures could be reduced or eliminated. Based on the insight presented above, one method would be to increase the grain size in the deposited film. From the previous section, we established that vertical nanostructures form predominantly at GBs. It then follows that larger grains would lead to a lower density of GBs and, in turn, a decrease in the areal density of vertical nanostructures. A second method could be to remove vertical nanostructures through physical or chemical means. Physical sputtering and chemical etching of vertical nanostructures are two pathways that could be employed during or after deposition to remove vertical nanostructures. Because of reduced atomic coordination, the edges of the vertical nanostructures are highly reactive when compared to the basal planes and thus could be preferentially removed. A third method may be post-deposition, high-temperature annealing to force the vertical nanostructures to realign parallel to the substrate, the more thermodynamically stable state. However, this method risks incompatibility with BEOL processes.

Recently, plasma treatments during or after deposition have been reported to enhance the grain size in thin films. Various plasma gas compositions, from chemically inert to highly reactive, have been used to affect this change. Kim et al. demonstrated the efficacy of a chemically inert Ar plasma in a post-deposition treatment to enhance the grain size in SnS2 films by physical sputtering of surface atoms. On the other hand, Macco et al. reported the use of a reactive plasma during ALD for grain size enhancement in zinc oxide thin films. The H2 plasma was proposed to chemically etch some nucleating sites, resulting in a lower nucleation site density on the surface. The lower nucleation density allowed for increased lateral growth of the established grains. These reports suggest that a plasma treatment can be a suitable method to suppress vertical nanostructure formation. Thus, we considered plasma treatments both during and after ALD growth. The results of the plasma treatments obtained during ALD are discussed first here.

To investigate the impact of plasma treatments on vertical nanostructure suppression during ALD, we implemented an additional plasma exposure step to our previously established WS2 PEALD process. This additional plasma treatment was incorporated into our “AB” PEALD process as a third step to form a three-step “ABC” process. These processes are designated by an ABC-type naming system: AB for the standard PEALD process, ABCAr when an Ar plasma step C was used, and ABCH2 when a H2 plasma step C was used. Depositions were performed using AB and ABC processes at 450 °C unless stated otherwise, as the film resistivity was lowest at this temperature in the investigated temperature range (100–450 °C, Table S2).

The impact of the Ar and H2 plasma exposure on the areal density of the vertical nanostructures was investigated by HAADF-STEM images. Figure 5 shows top-view, low-magnification (500k×) HAADF STEM images of WS2 films...
density of vertical nanostructures was determined from multiple measurements on high-magnification HAADF-STEM images (image area $\approx 380 \times 380$ nm$^2$). The average areal density was determined to be $\approx 706$ nanostructures per $\mu$m$^2$ in the case of the AB process, which reduced substantially by $\approx 80\%$ to $\approx 145$ nanostructures per $\mu$m$^2$ for the ABC$_{Ar}$ process. In the case of the ABC$_{H_2}$ process, the average areal density reduced by $\approx 29\%$ to $\approx 504$ nanostructures per $\mu$m$^2$. The absence of vertical nanostructures in the cross-sectional STEM images further corroborates their suppression with the ABC$_{Ar}$ process. In the ABC$_{H_2}$ process, the average areal density increased to $\approx 24$ nanostructures per $\mu$m$^2$. The AB$_{H_2}$ process showed a significant increase in the areal density of vertical nanostructures, identified by brighter contrast and lattice lines in some cases, which is reduced significantly by both the ABC$_{Ar}$ and ABC$_{H_2}$ processes relative to the AB process (Figure 5a). This reduction in areal density appeared to be larger with the ABC$_{Ar}$ process on initial inspection and was then confirmed by quantifying the average areal density of the vertical nanostructures, as shown in Table 1. The average areal density enabled by grain size enhancement alone. However, estimating the reduction in GB density resulting from grain size enhancement could enable us to ascertain the degree of suppression in vertical nanostructure areal density enabled by grain size enhancement alone. Assuming random grain orientation angles, the vertical area density of GBs for the AB, ABC$_{Ar}$, and ABC$_{H_2}$ processes (Table 1) were determined from multiple grain measurements on high-magnification HAADF-STEM images (Figure S6 and Table S3). Because of the poor visibility of the grains and their boundaries in the atomic resolution images, grain size measurements were carried out using a live FFT in Digital Micrograph software to establish all edges of the measured grains. The average grain size was determined to be $13.6$ nm for the reference AB process. For both the ABC$_{Ar}$ and ABC$_{H_2}$ processes, an enhancement in the lateral grain size was observed with respect to the AB process (Table 1). The grain size enhancement was substantial for the ABC$_{Ar}$ process, wherein the average grain size increased to $\approx 24$ nm, a $76\%$ increase. For the ABC$_{H_2}$ processes, the grain size enhancement was less substantial, wherein the grain size increased to $\approx 19$ nm, a $40\%$ increase. These results demonstrate that both Ar and H$_2$ plasma treatments induce considerable grain size enhancements that contribute to an effective reduction in the areal density of vertical nanostructures (Figure 5).

The grain size enhancements induced by the plasma treatments can arise from various plasma–surface interactions depending upon the constituents of the plasma. The ions in the chemically inert Ar plasma are known to influence growth and material properties in thin films exclusively through physical effects. Through ion bombardment, the energetic ions transfer energy and momentum to the growth surface. Depending upon the kinetic energy of ions, Ar ion bombardment on the growth surface can lead to several physical effects including adatom migration, desorption of physically adsorbed species, displacement of lattice atoms in the substrate and bulk, sputtering, subsurface or bulk implantation of ions or displaced atoms, etc. The MeV energy of Ar ions used in our PEALD process was measured to be $\approx 12$ eV using a retarding field energy analyzer (RFEA) (Figure S7). At these low ion energies, ion implantation during Ar plasma exposure in step C from or to the WS$_2$ surface, is highly unlikely to occur. The ion energy is on the borderline for mild sputtering of S atoms. Therefore, adatom migration and displacement of lattice atoms in the laterally oriented grains are most likely to ensue. These physical effects can cause structural rearrangements on the growth surface, which subsequently may lead to an enhancement in the grain size.

The use of a reactive H$_2$ plasma entails both ion–surface and radical–surface interactions having physical and chemical components. Because of its low mass, H ions are very unlikely to contribute to physical effects through momentum transfer. On the other hand, reactive species in the H$_2$ plasma, for example, radicals, have been reported to influence a wide range of properties (including grain size) in thin films growing through various processes. The H$_2$ plasma in step C can etch away isolated/unstable nucleating sites on the WS$_2$ surface, thereby reducing the nucleation density and allowing established grains to continue expanding laterally.

Estimating the degree of suppression in vertical nanostructure areal density enabled by grain size enhancement is not straightforward. However, estimating the reduction in GB density resulting from grain size enhancement could enable us to ascertain the degree of suppression in vertical nanostructure areal density enabled by grain size enhancement alone. Assuming random grain orientation angles, the vertical areal nanostructure density should follow a linear relationship with the GB density. Here, we used a Voronoi grain-based model to estimate the density of GBs for the AB, ABC$_{Ar}$, and ABC$_{H_2}$ processes based on the average grain size (see Supporting Information—Table S4). Using this model, we would expect a $68 \pm 5\%$ reduction in GB density for the observed grain size increase of $76 \pm 8\%$ for the ABC$_{Ar}$ process (grain size reported in Table 1). Similarly, we expect a $46 \pm 3\%$ GB density reduction for the observed grain size increase of $40 \pm 3\%$ for the ABC$_{H_2}$ process. Following a linear relationship assumption, the areal density of vertical nanostructures should also be suppressed by similar degrees, suggesting that the suppression of vertical nanostructures should predominantly arise from grain size enhancements.
From Table 1, the reduction in areal density of vertical nanostructures was determined to be 80 ± 10% for the ABC$_{Ar}$ process and 29 ± 3% for the ABC$_{H_2}$ process, relative to the AB process. For the ABC$_{Ar}$ process, the experimentally determined reduction (80%) is larger than the expected reduction from the model (68%). Grain size enhancement accounts for a significant portion of vertical nanostructure suppression; however, deviation from the one-to-one correlation suggests that there could be suppression contribution from other physicochemical effects. Conversely, the ABC$_{H_2}$ process exhibits a lower vertical nanostructure suppression (29%) than the reduction expected from the model (46%). This suggests that grain size enhancement does significantly contribute to the suppression of vertical nanostructures but seems to be significantly offset by physicochemical effects. The hydrogen in the plasma may promote the growth of vertical nanostructures during plasma–surface interactions, partially mitigating suppression from grain size enhancement. Thus, it is apparent that grain size enhancement alone cannot fully account for vertical nanostructure suppression and other physicochemical effects, such as etching of S atoms, thermal annealing effects, and so forth, may play an important role. This warrants a further investigation, and we discuss this below.

**Etching of S Atoms.** Besides aiding grain size enhancement, plasma–surface interactions can occur directly at the formation sites of vertical nanostructures. These interactions may be instrumental in mitigating the vertical nanostructure formation during the deposition of WS$_2$. The two plasmas, however, may interact with the surface in very different ways.

Beyond the reaction with surface nuclei, the reactive species in the H$_2$ plasma can also react with the established surface. We have recently shown that an abundance of H species in a H$_2$ diluted H$_2$S plasma will react with WS$_2$ surfaces, leading to S atom removal. Because of their higher reactivity, the edge atoms are more vulnerable to plasma etching than the relatively inert basal planes and are likely to be preferentially etched. In this work, exposure to H$_2$ plasma in step C can etch the edge-determined vertical nanostructures that begin to form at GBs during the preceding AB steps in every ALD cycle. The relatively thinner vertical nanostructures observed in Figure 5c may be a consequence of H$_2$ plasma etching, an aspect not observed with the AB or ABC$_{Ar}$ processes (Figure 5a,b). In addition, H$_2$ plasma exposure results in more S-deficient WS$_2$ lateral and vertical nanostructure edges (S/W = 1.6, Table 1).

Importantly, Azizi et al. have shown that S-deficient dislocations at GBs result in higher dislocation mobility along grain edges. As stated earlier (see "Formation of Vertical WS$_2$ Nanostructures"), higher dislocation or defect mobility at grain edges may significantly impact the formation of vertical nanostructures. This could be attributed to surface/edge reconstruction during deposition, mitigating the formation of vertical nanostructures. Hence, the etching of S atoms from edge sites could play an important role in the suppression of vertical nanostructure formation. However, tungsten precursor adsorption (step A) is also more energetically favorable on such S-deficient surfaces, leading to enhanced growth rates (Figure S2 and Table S1). This competition between vertical nanostructure formation and etching may limit the etching effect induced by the H$_2$ plasma as film growth proceeds. The reduced etching effect seems to limit grain size enhancements. These effects may explain the significant deviation observed in vertical nanostructure suppression determined experimentally and from the model (Table S4).

On the other hand, an Ar plasma does not have a similar level of reactivity as a H$_2$ plasma. Thus, chemical etching is not the likely outcome from the interaction of Ar ions with the WS$_2$ surface, although vertical nanostructure suppression is observed to be more significant from Ar plasma exposure than from H$_2$ plasma exposure. The significantly higher mass of Ar ions as compared to hydrogen ions most likely plays a key role in the effect of surface bombardment during plasma exposure. The higher energy imparted to the surface from the heavier Ar$^+$ may be responsible for stronger surface reconstruction at defect/dislocation and edge sites. Komsa et al. calculated displacement energy thresholds for WS$_2$, revealing a lower required energy for edge-site displacement. These calculations corroborate the "preference" for edge-site reconstruction versus surface reorganization. Surface/edge reconstruction from Ar$^+$ bombardment may have the same, yet a more pronounced, end result as with H$_2$ plasma exposure: edge reconstruction, resulting in the suppression of vertical nanostructures. Although vertical nanostructure formation is suppressed with both plasmas, the two processes seem to affect this change through two different physicochemical pathways.

The effect of plasma was further investigated by comparing the ABC process, as discussed above, to an AB process with a plasma treatment after finishing the ALD growth (Figure S8). These post-ALD plasma exposure processes are referred to as AB$_{post-Ar}$ plasma when an Ar plasma was used or AB$_{post-H_2}$ plasma when H$_2$ plasma was used. The areal density of vertical nanostructures did not vary significantly between the reference AB and the AB$_{post-plasma}$ processes with Ar or H$_2$ plasma. This clearly indicates that the post-ALD plasma exposures are not efficient in suppressing the growth of the well-established vertical nanostructures. In hindsight, the etching of S atoms by H$_2$ plasma is limited to the top edges of vertical nanostructures. Downward etching of the vertical nanostructures would involve the complete removal of S and W atoms from layers, which would not be possible with the H$_2$ plasma used. Thus, the etching and thereby the surface/edge reconstruction are limited to the top edges of vertical nanostructures, and consequently, no significant reduction in the areal density of vertical nanostructures is observed because of post-growth plasma exposure. A similar behavior can also be expected in the case of Ar plasma, where the surface/edge reconstruction enabled by Ar$^+$ bombardment because of displacement of atoms is limited on the well-established vertical nanostructures. Therefore, these findings emphasize that the suppression of the vertical nanostructures through plasma exposure is more effective during the nucleation of vertical nanostructures when compared to their established growth.

**Thermal Annealing during Deposition.** The total deposition time of the ABC processes was ∼1 h longer than the AB process because of the additional step C (duration = 50 s per cycle). This means that the samples in the ABC process underwent extra processing time at the deposition temperature (450 °C). In addition, this extra processing time may induce thermal annealing effects that can influence the structural profile of the films, including the areal density of vertical nanostructures. Thermal energy from annealing can cause surface restructuring via diffusion of the constituents, resulting in
in the morphology that is known to be most thermodynamically favorable, that is, a film with horizontally aligned basal planes exclusively.\(^9\) Oh et al. have reported a similar observation when the temperature was increased during the post-sulfurization of ALD-deposited MoS\(_2\) films.\(^5\) To investigate the effect of annealing on the areal density of vertical nanostructures, the Ar plasma exposure in step C was replaced by an Ar gas exposure. Ar gas exposure in step C should not influence the film growth as it does not entail any physical effects such as ion bombardment unlike an Ar plasma exposure. Hence, thermal annealing effects introduced by step C, if any, could be determined by comparing the areal density of vertical nanostructures resulting from ABC\(_{\text{gas}}\) and ABC\(_{\text{plasma}}\) processes.

**GB Angle.** From the formation studies, we established that vertical nanostructures in the AB process predominantly form at low-angle GBs with an average misorientation angle of \(\sim 5.6^\circ\) (Figure 4). We then investigated if the misorientation angles at GBs without vertical nanostructures were influenced by the Ar or H\(_2\) plasma exposure in step C of the ABC processes. Variation in the misorientation angle could have led to a reduction or increase in the areal density of vertical nanostructures if the average misorientation angle was higher or lower, respectively.

Grain misorientation angles were studied from HAADF-STEM images of the AB, ABC\(_{\text{Ar}}\), and ABC\(_{\text{H}}\) processes. For a comprehensive study, 50 GBs for the AB process and 47 GBs for both ABC processes were examined. The abundance of misorientation angles by the process is presented in Figure 7.

**Figure 6.** Top-view HAADF-STEM images of WS\(_2\) films synthesized using (a) AB, (b) ABC\(_{\text{Ar}}\), and (c) ABC\(_{\text{Ar-plasma}}\) processes.

An initial inspection of the data does not reveal any obvious differences between the AB and ABC processes. The average misorientation angle from each process (17.1\(^\circ\) for AB, 17.0\(^\circ\) for ABC\(_{\text{Ar}}\), and 16.7\(^\circ\) for ABC\(_{\text{H}}\)) confirms that there is no significant variation with plasma exposure in step C. This suggests that the orientation angles are determined in the very early stages of nucleation, where all nuclei can be treated independently and can adopt all possible rotational orientations around the normal to the 2D layers.

In summary, grain size enhancement is the major factor enabling the suppression of vertical nanostructures. Other physicochemical effects such as etching of S atoms, thermal annealing, and so forth have smaller contributions.

**Figure 7.** Abundance of misorientation angles without vertical nanostructures by sample: AB (red), ABC\(_{\text{Ar}}\) (blue), and ABC\(_{\text{H}}\) (orange).

**Impact of Combining Ar and H\(_2\) Plasma Gas Mixtures (in Step C) on the Suppression of Vertical Nanostructures.** Both Ar and H\(_2\) plasma exposures led to a reduction in the density of vertical nanostructures per geometric area in WS\(_2\) films through physicochemical effects (Figure 5b,c). When combined, a plasma exposure could exhibit the reduction qualities of both individual plasmas, resulting in a cooperative effect. In principle, the ion bombardment of ions in the Ar plasma coupled with the high reactivity of plasma species in the H\(_2\) plasma could lead to a further reduction of the areal density of vertical nanostructures. Cooperative effects of the Ar and H\(_2\) plasma on the areal density of vertical
nanostructures were investigated by gradually mixing the Ar and H2 plasma gases in step C (process = ABCAr+H2).

Figure 8 shows a series of top-view HAADF-STEM images of WS2 films (~6 nm) synthesized using the ABCAr, ABCAr+H2, and ABCH2 processes. In this series, gas flow rates were decreased or increased by a 10 sccm increment for Ar or H2, respectively. With the addition of just 10 sccm H2 to the Ar plasma gas, noticeable changes are observed in the areal density and the appearance of the vertical nanostructures (Figure 8b). The vertical nanostructures were relatively thinner, and their appearance was much closer to that observed for ABCH2 (Figure 8e), showing that a small addition of H2 to the plasma gas has an immediate effect. Interestingly however, the addition of H2 did not decrease the areal density of vertical nanostructures, rather an increase was observed. This increase in areal density continued in a nearly linear fashion with the increase of H2/decrease of Ar in the plasma. Table 2 shows the areal density of vertical nanostructures with plasma gas modulation determined from multiple measurements on high-magnification HAADF-STEM images of WS2 (image area = 380 × 380 nm² area).

Apart from causing a reduction in the areal density of vertical nanostructures, the plasma exposure in step C had a significant impact on the film stoichiometry (S/W) and resistivity. Figure 9 compares the film stoichiometry (S/W, determined by XPS, left y-axis) and the resistivity (determined by 4-PP, right y-axis) for the AB, ABCAr, ABCAr+H2, and ABCH2 processes. The AB and ABCAr processes yielded nearly stoichiometric (S/W = ~2) films (see Figure S9 for raw XPS data). Upon the addition of H2 to the Ar plasma, a decrease in stoichiometry was observed. The S/W ratio decreased to approximately 1.7 in all of the ABCAr+H2 processes as seen from the center points of Figure 9. Eliminating Ar from the plasma gas mixture further decreased the S/W ratio to 1.6 for the ABCH2 process. This significant change in the S/W ratio shows that the presence of H2 species in the plasma removes S atoms from the growth surface corroborating the surface etching discussed above.

The resistivity of a WS2 film (~6 nm) deposited by the AB process was found to be approximately 10^5 Ω·cm. With the addition of the plasma step C, the resistivities of films synthesized with the various ABC processes were found to be an order of magnitude lower (~10^5 Ω·cm) when compared to the AB process. This decrease in resistivity can be attributed to several factors, and we discuss them below.

### Table 2. Average Areal Density of Vertical Nanostructures per Geometric Area Determined from Multiple Measurements on HAADF-STEM Images of WS2 Deposited Using the ABCAr, ABCAr+H2, and ABCH2 Processes

| PEALD process | Ar/H2 flow (sccm) | Areal density of vertical nanostructures (per µm²) |
|---------------|-------------------|-----------------------------------------------|
| ABCAr         | 40:00             | ~145 ± 14                                     |
| ABCAr+H2      | 30:10             | ~252 ± 27                                     |
| ABCAr+H2      | 20:20             | ~308 ± 34                                     |
| ABCH2         | 10:30             | ~399 ± 35                                     |
| ABCH2         | 00:40             | ~504 ± 41                                     |

The observed plasma–surface interactions to act more similarly to a pure H2 plasma. The chemical reactivity of H2 species in the plasma seems to overshadow the physical effects enabled by Ar plasma (adatom migration, displacement of lattice S atoms, etc.), which could play a key role in suppressing the growth of vertical nanostructures as discussed earlier (see “Grain Size Enhancement” and “Etching of S Atoms”). Coupled to this, the hydrogen species may lower the diffusivity of constituents on the growth surface (S-atoms) enabled by the Ar ion bombardment and thus reduce the impact of the physical effects such as adatom migration, displacement of lattice S atoms, and so forth. At the same time, the growth rate and density of vertical nanostructures are higher on S-deficient surfaces enabled by the H2 species in the plasma, as discussed earlier (see "Etching of S Atoms"). Thus, we see an increase in the areal density of vertical nanostructures for the ABCAr+H2 processes. Furthermore, the nearly linear increase in vertical nanostructure areal density with the modulation of the plasma gas composition from Ar to Ar + H2 to H2 reveals an absence of any cooperative effect between the generated plasma species.

### Impact of Plasma Exposure (Step C) on Other Material Properties

Apart from causing a reduction in the areal density of vertical nanostructures, the plasma exposure in step C had a significant impact on the film stoichiometry (S/W) and resistivity. Figure 9 compares the film stoichiometry (S/W, determined by XPS, left y-axis) and the resistivity (determined by 4-PP, right y-axis) for the AB, ABCAr, ABCAr+H2, and ABCH2 processes. The AB and ABCAr processes yielded nearly stoichiometric (S/W = ~2) films (see Figure S9 for raw XPS data). Upon the addition of H2 to the Ar plasma, a decrease in stoichiometry was observed. The S/W ratio decreased to approximately 1.7 in all of the ABCAr+H2 processes as seen from the center points of Figure 9. Eliminating Ar from the plasma gas mixture further decreased the S/W ratio to 1.6 for the ABCH2 process. This significant change in the S/W ratio shows that the presence of H2 species in the plasma removes S atoms from the growth surface corroborating the surface etching discussed above.

The resistivity of a WS2 film (~6 nm) deposited by the AB process was found to be approximately 10^5 Ω·cm. With the addition of the plasma step C, the resistivities of films synthesized with the various ABC processes were found to be an order of magnitude lower (~10^5 Ω·cm) when compared to the AB process. This decrease in resistivity can be attributed to several factors, and we discuss them below.
The reduced areal density of vertical nanostructures observed for the ABC processes (Table 2) could directly contribute to the observed decrease in film resistivity because of the following reasons. First, the electrical resistivity perpendicular, ($\parallel$), to the layers is known to be about twice the resistivity within the layers, ($\perp$).42,43 Thus, the presence of vertical nanostructures amidst basal-plane-oriented layers may cause a rise in film resistivity. Second, the vertical nanostructures can cause scattering of mobile charge carriers as the vertical nanostructures were observed right from the film nucleation regime (Figure S5). This effect is elucidated by the comparatively low film resistivity observed in the nucleation stage for the ABC processes (Figure S10). In the nucleation stage, the ABC processes had lower areal density of vertical nanostructures when compared to the AB process as discussed before (Figure S5). In this context, the presence of such vertical nanostructures amidst the basal-plane-oriented layers is highly undesirable for obtaining films with low resistivity.

Film doping induced by the S-deficiencies (S/W < 2) from the ABCAr+H2 and ABCAr processes (Figure 9) may contribute to the decrease in film resistivity. On the other hand, the areal density of vertical nanostructures (Figure 8), a relatively higher film resistivity was anticipated for the ABCAr+H2 and ABCAr processes when compared to the ABCAr process. However, the film resistivity did not vary significantly between the ABCAr, ABCAr+H2, and ABCAr processes. Film doping induced by the S-deficiencies observed with the ABCAr+H2 and ABCAr processes (Table 2) seems to lower film resistivity and compensate for the presence of the relatively higher areal density of vertical nanostructures. Tungsten disulfide films exhibiting acute S-deficiencies (WS1.6) have typically been associated with n-type doping.46,47

The grain size enhancement observed previously for the ABC processes (Table 1) may also contribute to the lowered resistivity of the films. Larger grains result in a lower number of GBs, which may result in less charge scattering at GBs. Furthermore, thermal annealing effects from increased deposition time in the ABC processes can have small contributions to the drop in film resistivity. The resistivity of films deposited using the ABCAr processes (Figure 6—ABCAr processes) was observed to be lower when compared to the reference AB process, as shown in Figure S11. However, the drop in resistivity induced by thermal annealing effects is minor when compared to the plasma-induced drop in resistivity.

We believe that the vertical structure formation pathways and mechanism discussed here can be generalized to other 2D TMDs grown using ALD. Because of the growth similarities, we believe that we can safely relate vertical nanostructure suppression in ALD WS2 shown in our work to other TMDs. Beyond ALD growth, plasma-based treatments can be included along with other growth techniques (during or post growth) to induce physical changes. It is noteworthy to mention that such changes would be strongly dependent on the plasma parameters.

### CONCLUSIONS

In conclusion, we discussed formation pathways for the growth of vertical 3D WS2 nanostructures and introduced an approach to effectively suppress their growth during PEALD. We established formation pathways for the vertical nanostructures, and through extensive STEM studies, we demonstrated how these nanostructures originate at GBs. The formation pathway insights obtained in this work improve the current level of understanding of the vertical nanostructure growth reported in the literature. For suppressing the growth of vertical nanostructures, we introduced a new low-temperature PEALD process. This process effectively suppresses the growth of vertical 3D nanostructures during the growth of 2D WS2 layers by incorporating additional plasma treatment steps in the PEALD cycles. By adding the plasma treatment steps, the GB density drastically decreased, which together with other physicochemical effects of the plasma led to an 80% reduction of the vertical nanostructure density relative to its original value. As a consequence, the resistivity of the films reduced by an order of magnitude. The observed relation between the GB density and vertical nanostructures will lay the foundation for further studies on vertical nanostructure suppression, not only during ALD but also during other commonly used 2D TMD growth techniques such as CVD. The established growth pathways and our approach to vertical nanostructure suppression during PEALD will likely extend to other 2D TMD systems.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b19716.

WS2 PEALD saturation curves; PEALD growth behavior of AB, ABCAr, and ABCAr processes; propagation and expansion of vertical structures; temperature-dependent WS2 film resistivity of AB process; cross-sectional STEM images of WS2 films; nucleation phase of WS2 films; grain size determination from STEM images; estimating the reduction in the areal density of OoPO structures enabled by grain size enhancement; ion energies of Ar and H2 plasma used; suppression of vertical nanostructures via plasma exposure after ALD film growth; XPS analysis of WS2 films; and film resistivity: AB versus ABC processes (PDF)
Notes
The authors declare no competing financial interest.

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References
(1) Fiori, G.; Bonaccorso, F.; Iannaccone, G.; Palacios, T.; Neumaier, D.; Seabaugh, A.; Banerjee, S. K.; Colombo, L. Electronics Based on Two-Dimensional Materials. Nat. Nanotechnol. 2014, 9, 768−779.
(2) Chhowalla, M.; Jena, D.; Zhang, H. Two-Dimensional Semiconductor Nanosheets for Transistors. Nat. Rev. Mater. 2016, 1, 16052.
(3) Schram, T.; Smets, Q.; Groven, B.; Heyne, M. H.; Kunnen, E.; Thian, A.; Devriendt, K.; Delabie, A.; Lin, D.; Lux, M.; Chiappe, D.; Asselberghs, L.; Brus, S.; Huyghenbaert, C.; Sayan, S.; Juncker, A.; Caymax, M.; Radu, I. P. WS2 Transistors on 300 mm Wafers with BEOL Compatibility. In 2017 47th European Solid-State Device Research Conference (ESSDERC); IEEE, 2017; pp 212−215.
(4) Browning, R.; Plachinda, P.; Padigi, P.; Solanki, R.; Rouvimov, S. Growth of Multiple WSe2/SnSe2 Layered Semiconductor Heterojunctions. Nanoscale 2016, 8, 2143−2148.
(5) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. Nat. Nanotechnol. 2012, 7, 699−712.
(6) Choi, W.; Choudhary, N.; Han, G. H.; Park, J.; Akinwande, D.; Lee, Y. H. Recent Development of Two-Dimensional Transition Metal Dichalcogenides and Their Applications. Mater. Today 2017, 20, 116−130.
(7) Gutiérrez, H. R.; Pereir-Lópe, N.; Elias, L.; Berkdemir, A.; Wang, B.; Lv, R.; López-Urías, F.; Crespi, V. H.; Terrones, H.; Terrones, M. Extraordinary Room-Temperature Photoluminescence in Triangular WS2 Monolayers. Nano Lett. 2013, 13, 3447−3454.
(8) Groven, B.; Nalin Melta, A.; Bender, H.; Meerschaut, J.; Nuytten, T.; Verdonck, P.; Conard, T.; Smets, Q.; Caymax, M.; Schoenaers, B.; Steensma, A.; Afanas’ev, V.; Vandervorst, W.; Heyns, M.; Caymax, M.; Radu, I.; Delabie, A. Two-Dimensional Crystal Grain Size Tuning in WS2 Atomic Layer Deposition: An Insight in the Nucleation Mechanism. Chem. Mater. 2018, 30, 7648−7663.
(9) Oh, S.; Kim, J. B.; Song, J. T.; Oh, J.; Kim, S.-H. Atomic Layer Deposition Molybdenum Disulfide on Si Photocathodes for Highly Efficient Photoelectrochemical Water Reduction Reaction. J. Mater. Chem. A 2017, 5, 3304−3310.
(10) Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D. C. B.; Fujita, T.; Chen, M.; Asea, T.; Shenoy, Y. B.; Eda, G.; Chhowalla, M. Enhanced Catalytic Activity in Strained Chemically Exfoliated WS2 Nanosheets for Hydrogen Evolution. Nat. Mater. 2015, 14, 850−855.
(11) Li, H.; Wu, J.; Yin, Z.; Zhang, H. Preparation and Applications of Mechanically Exfoliated Single-Layer and Multilayer MoS2 and WSe2 Nanosheets. Acc. Chem. Res. 2014, 47, 1067−1075.
(12) Jeon, J.; Jang, S. K.; Jeon, S. M.; Yoo, G.; Jang, Y. H.; Park, J.; H.; Lee, S. Layer-Controlled CVD Growth of Large-Area Two-Dimensional MoS2 Films. Nanoscale 2015, 7, 1688−1695.
(13) Zhang, Y.; Zhang, Y.; Ji, Q.; Ju, J.; Yuan, H.; Shi, J.; Gao, T.; Ma, D.; Liu, M.; Chen, Y.; Song, X.; Huang, H. Y.; Cui, Y.; Liu, Z. Controlled Growth of High-Quality Monolayer WS2 Layers on Sapphire and Imaging Its Grain Boundary. ACS Nano 2013, 7, 8963−8971.
(14) Pawbake, A. S.; Pawar, M. S.; Jadkar, S. R.; Late, D. J. Large Area Chemical Vapor Deposition of Monolayer Transition Metal Dichalcogenides and Their Temperature Dependent Raman Spectroscopy Studies. Nanoscale 2016, 8, 3008−3018.
(15) Li, H.; Wu, H.; Yuan, S.; Qian, H. Synthesis and Characterization of Vertically Standing MoS2 Nanosheets. Sci. Rep. 2016, 6, 21171.
(16) Kong, D.; Wang, H.; Cha, J. J.; Pasta, M.; Koski, K. J.; Yao, J.; Cui, Y. Synthesis of MoS2 and MoSe2 Films with Vertically Aligned Layers. Nano Lett. 2013, 13, 1341−1347.
(17) Jung, Y.; Shen, J.; Liu, Y.; Woods, J. M.; Sun, Y.; Cha, J. J. Metal Seed Layer Thickness-Induced Transition From Vertical to Horizontal Growth of MoS2 and WS2. Natl. Nanotechnol. 2014, 14, 6842−6849.
(18) Lin, Y.-C.; Zhang, W.; Huang, J.-K.; Liu, K.-K.; Lee, Y.-H.; Liang, C.-T.; Chu, C.-W.; Li, L.-J. Wafer-Scale MoS2 Thin Layers Prepared by MoO3 Sulfurization. Nanoscale 2012, 4, 6637.
(19) Woods, J. M.; Jung, Y.; Xie, Y.; Liu, W.; Liu, Y.; Wang, H.; Cha, J. J. One-Step Synthesis of MoS2/WS2 Layered Heterostructures and Catalytic Activity of Defective Transition Metal Dichalcogenide Films. ACS Nano 2016, 10, 2004−2009.
(20) Muratore, C.; Hu, J.; Wang, B.; Haque, M. A.; Bultman, J. E.; Jespersen, M. L.; Shamberger, P. J.; McConney, M. E.; Nagyu, R. D.; Voevodin, A. A. Continuous Ultra-Thin MoS2 Films Grown by Low-Temperature Physical Vapor Deposition. Appl. Phys. Lett. 2014, 104, 261604.
(21) Tao, J.; Chai, J.; Lu, X.; Wong, L. M.; Wong, T. I.; Pan, J.; Xiong, Q.; Chi, D.; Wang, S. Growth of Wafer-Scale MoS2 Monolayer Prepared by MoO3 Sulfurization. Nanoscale 2016, 7, 2497−2503.
(22) Li, Q.; Newberg, J. T.; Walter, E. C.; Hemminger, J. C.; Penner, R. M. Polycrystalline Molybdenum Disulfide (2H-MoS2) Nano- and Microribbons by Electrochemical/Catalytic Synthesis. Nano Lett. 2007, 7, 277−281.
(23) Valappil, M. O.; Anil, A.; Shajumon, M.; Pillai, V. K.; Alwarappan, S. A Single-Step Electrochemical Synthesis of Luminescent WS2 Quantum Dots. Chem. Eur. J. 2017, 23, 9144−9148.
(24) Tan, L. K.; Liu, B.; Teng, J. H.; Guo, S.; Low, H. Y.; Loh, K. P. Atomic Layer Deposition of a MoS2 Film. Nano. Lett. 2014, 4, 10584−10588.
(25) Delabie, A.; Caymax, M.; Groven, B.; Heyne, M.; Jha, S.; Meereschaut, J.; Nuytten, T.; Bender, H.; Conard, T.; Verdonck, P.; Van Elshocht, S.; De Gendt, S.; Heyns, M.; Barla, K.; Radu, I.; Thean, A. Low Temperature Deposition of 2D WS2 Layers from WS6 and H2S Precursors: Impact of Reducing Agents. Chem. Commun. 2015, 51, 15692−15695.
(26) Hao, W.; Marichy, C.; Journet, C. Atomic Layer Deposition of Stable 2D Materials. 2D Mater. 2018, 6, 012001.
(27) Tan, L. K.; Liu, B.; Teng, J. H.; Guo, S.; Low, H. Y.; Loh, K. P. Atomic Layer Deposition of a MoS2 Film. Nano. Lett. 2014, 4, 10584−10588.
(28) Puurunen, P. L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/Water Process. J. Appl. Phys. 2005, 97, 121301.
(29) George, S. M. Atomic Layer Deposition: An Overview. Chem. Rev. 2010, 110, 111−131.
(30) Prodi, H. B.; Potts, S. E.; van de Sanden, M. C. M.; Kessels, W. M. M. Plasma-Assisted Atomic Layer Deposition: Basics, Opportunities, and Challenges. J. Vac. Sci. Technol. A 2011, 29, 050801.
(31) Bilyk, N.; Haider, A. Atomic Layer Deposition: An Enabling Technology for the Growth of Functional Nanoscale Semiconductor. Semicond. Sci. Technol. 2017, 32, 093002.
(66) Komsa, H.-P.; Kotakoski, J.; Kurasch, S.; Lehtinen, O.; Kaiser, U.; Krasheninnikov, A. V. Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping. Phys. Rev. Lett. 2012, 109, 035503.
(67) Regula, M.; Ballif, C.; Moser, J. H.; Lévy, F. Structural, Chemical, and Electrical Characterisation of Reactively Sputtered WSx Thin Films. Thin Solid Films 1996, 280, 67–75.
(68) Cong, C.; Shang, J.; Wu, X.; Cao, B.; Peimyoo, N.; Qiu, C.; Sun, L.; Yu, T. Synthesis and Optical Properties of Large-Area Single-Crystalline 2D Semiconductor WSx Monolayer from Chemical Vapor Deposition. Adv. Opt. Mater. 2014, 2, 131–136.