Area-Selective Atomic Layer Deposition of Two-Dimensional WS₂ Nanolayers
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ABSTRACT: With downscaling of device dimensions, two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) such as WS₂ are being considered as promising materials for future applications in nanoelectronics. However, at these nanoscale regimes, incorporating TMD layers in the device architecture with precise control of critical features is challenging using current top-down processing techniques. In this contribution, we pioneer the combination of two key avenues in atomic-scale processing: area-selective atomic layer deposition (AS-ALD) and growth of 2D materials, and demonstrate bottom-up processing of 2D WS₂ nanolayers. Area-selective deposition of WS₂ nanolayers is enabled using an ABC-type plasma-enhanced ALD process involving acetylacetone (Hacac) as inhibitor (A), bis(tert-butylimido)-bis(dimethylamido)-tungsten as precursor (B), and H₂S plasma as the co-reactant (C) at a low deposition temperature of 250 °C. The developed AS-ALD process results in the immediate growth of WS₂ on SiO₂ while effectively blocking growth on Al₂O₃ as confirmed by in situ spectroscopic ellipsometry and ex situ X-ray photoelectron spectroscopy measurements. As a proof of concept, the AS-ALD process is demonstrated on patterned Al₂O₃/SiO₂ surfaces. The AS-ALD WS₂ films exhibited sharp Raman (E₂g and A₁g) peaks on SiO₂, a fingerprint of crystalline WS₂ layers, upon annealing at temperatures within the thermal budget of semiconductor back-end-of-line processing (≤450 °C). Our AS-ALD process also allows selective growth on various TMDs and transition metal oxides while blocking growth on HfO₂ and TiO₂. It is expected that this work will lay the foundation for area-selective ALD of other 2D materials.

The downscaling of dimensions in nanoelectronic devices has led to the exploration of alternate, two-dimensional (2D) semiconductors for future nanodevice applications.1–6 In this regard, semiconducting transition metal dichalcogenides (TMDs) such as WS₂ have attracted much interest, because of their high carrier mobility and direct bandgap in the monolayer regime.3,7 In ultra-scaled nanoelectronic devices, it is crucial to precisely incorporate TMD layers at desired locations in the device architecture with consistent layer characteristics. Conventionally, lithography-based top-down processing techniques are used to pattern films into device features. Precise patterning and alignment of critical device features will become challenging using the current top-down processing schemes especially in sub-5 nm technology nodes.8–10 At the same time, patterning 2D TMD layers with resist-based lithography risks inducing contaminants into the layers, that can significantly impact their functional characteristics.11–14 In this regard, selective growth of TMD layers on predetermined locations (also referred to as area-selective deposition) via bottom-up approaches has attracted significant interest from both academia and industry.14 Rather than performing deposition, lithography, and etching for each layer in a device stack, some of the layers can be incorporated in a bottom-up manner using this approach. By directly depositing TMD layers on prepatterned surfaces, area-selective deposition can enable the integration of TMD layers in multilayer device stacks without the need for resist-based patterning of the delicate TMD layers. Therefore, this approach decreases the total number of lithography and etching steps in the fabrication of nanoelectronic devices and, thus, can enable cost-effective device fabrication schemes for future technology nodes.

Area-selective deposition of TMD layers has been sparingly reported in the literature. Flakes of MoS₂ have been deposited at predetermined locations by using lithography-patterned
nucleation seeds or topological features in chemical vapor deposition (CVD) processes. In these reported methods, the removal of seeds after fabrication is not straightforward. The control over thickness and shape of the seeded TMD structures is also a point of concern. Area-selective growth of CVD MoS2 has also been enabled by enhancing the reactivity of predetermined areas to CVD surface reactions through chemical treatments and mechanically induced triboelectric effects. The use of seed layers were mitigated in these processes. However, the longevity and stability of the enhanced surface reactivity of predetermined areas is uncertain with these methods. Gallium ion beams have been used to control the density of surface hydroxyl groups on the initial substrate (SiO2) and achieve patterned growth of MoS2 in a CVD process. Recently, WS2 was selectively deposited using prepatterned a-Si sacrificial layers in a pulsed CVD process. Conceivably, to date, area-selective growth of TMD layers has remained unexplored. Ideally, an AS-ALD process should enable area-selective growth and, at the same time, offer the merits of conventional ALD processes including angstrom-level thickness control, uniform and conformal film growth over large-area substrates and high-aspect-ratio 3D structures, and low-temperature processing (typically T ≤ 450 °C). Therefore, there is considerable interest in developing AS-ALD processes for selectively depositing TMD layers.

Selective growth via AS-ALD can be realized by deactivating the non-growth area for a specific ALD chemistry. Select areas of the substrate can be functionalized with a blocking layer that allows growth only on the non-functionalized areas of the substrate. Self-assembled monolayers (SAMs) and small inhibitor molecules have been investigated as blocking agents in AS-ALD processes. Recently, Mameli et al. showcased the efficacy of vapor-phase dosed acetylacetonate inhibitor molecules (referred to as Hacac) in blocking precursor adsorption and thereby, blocking film growth on Al2O3 surfaces during AS-ALD of SiO2. The Hacac molecules were dosed every cycle, unlike the one-time application of SAMs in other AS-ALD processes, which makes the approach compatible with a wider range of processes, including plasma-enhanced ALD (PEALD). Taking a cue from these results, in this work, we use Hacac as an inhibitor to selectively deposit mono-to-multilayers of WS2.

![Figure 1. Schematic illustration of the WS2 area-selective ALD process using ABC-type ALD cycles. The Al2O3/SiO2 patterned surface is shown before, during, and after ALD. The individual ALD steps of the ABC-type ALD cycle are indicated: Step A, Hacac dose; Step B, bis(tert-butylimido)-bis(dimethylamido)-tungsten precursor dose; and Step C, H2S plasma exposure. Using this process, WS2 is selectively deposited on SiO2 in the presence of Al2O3.](https://dx.doi.org/10.1021/acsmaterialslett.0c00093)
such as MoS₂, NbS₂, and TiS₂ and (3) transition metal oxides such as MoO₃, Nb₂O₅, and WO₃ while effectively blocking growth on Al₂O₃ and HfO₂ surfaces at a low deposition temperature of 250 °C. We expect this first AS-ALD process for 2D WS₂, to enable exploration of area-selective ALD processes for other functional 2D materials.

A schematic of our AS-ALD approach is shown in Figure 1 for prepatterned Al₂O₃ (non-growth area) and SiO₂ (growth area) surfaces. It is based on a three-step (i.e., ABC-type) ALD process. In step A, we dose Hacac molecules that adsorb only on the Al₂O₃ surface and not on the SiO₂ surface. In step B, the precursor adsorption is blocked by the adsorbed Hacac inhibitor molecules on the Al₂O₃ surface, while the tungsten precursor (bis((tert-butylimido)-bis(dimethylamido)-tungsten) readily adsorbs on the SiO₂ surface. In the final step (step C), the H₂S plasma functions as the ALD co-reactant, enabling the growth of WS₂ on SiO₂. On the Al₂O₃ surface, it removes the adsorbed inhibitor molecules from the Al₂O₃ surface. Such ALD cycles are repeated to deposit WS₂ films selectively on SiO₂ surfaces. The BC steps of the ABC cycles used in this work were adopted from our previously reported WS₂ ALD process, which resulted in the growth of WS₂ films.42

Figure 2a shows the nucleation curves for the ABC-type WS₂ ALD process on SiO₂ (growth area) and Al₂O₃ (non-growth area), as determined from in situ spectroscopic ellipsometry (SE). The plot shows that WS₂ grows readily on SiO₂ surfaces without any growth delay. The film thickness increases linearly with the number of ALD cycles, a characteristic of the ALD growth behavior, with a growth per cycle (GPC) of ~0.6 Å. On the other hand, for the same ABC-type WS₂ ALD process on Al₂O₃, a growth delay of ~20 ALD cycles is observed. These results indicate that ~1 nm of WS₂ (at least one monolayer) can be selectively deposited on SiO₂ while blocking the growth on Al₂O₃. When performing BC cycles (without the use of Hacac), no growth delay was observed on Al₂O₃, as evidenced by a linear increase in thickness with the number of ALD cycles (see Figure S1 in the Supporting Information).

The nucleation behavior of our process was corroborated with X-ray photoelectron spectroscopy (XPS) measurements (Figure 2b and 2c). Consistent with the in situ SE data, the integrated area of the XPS W 4f peaks increased linearly with the number of ALD cycles on SiO₂, while a growth delay of ~20 ALD cycles was observed on Al₂O₃ (see Figures S2a−S2d in the Supporting Information for W and S XPS peak evolution). As shown in Figure 2c, distinct W 4f doublet peaks corresponding to WS₂ (W⁴⁺ oxidation state, binding energy ≈ 32.1 eV and 34.2 eV) were observed on the SiO₂ surface, whereas no W 4f core level (W⁺⁴) signals were observed on the Al₂O₃ surface after 20 ALD cycles. Note that the XPS detection limit for W on top of SiO₂ and Al₂O₃ was estimated to be <0.01 monolayer or ~2 × 10¹² atoms/cm². A film stoichiometry (S:W) of 2.3 was determined from XPS measurements on SiO₂ similar to our previous work.42 The binding energy of the XPS W 4f core levels (W 4f₇/₂ and W 4f₅/₂) appears to match those commonly observed for the 1T phase of WS₂.44 However, we have previously established the growth of a 2H phase of WS₂ layers for the same ALD process.
at a similar temperature (at 300 °C using XRD measurements). Therefore, we expect these layers to be in the 2H phase.

On SiO₂, the adsorption of Hacac molecules is known to be very minimal relative to Al₂O₃,²³ and, consistent with this, no growth delay was observed in this work as discussed above (see Figures 2a and 2b). Furthermore, XPS depth profiling of the WS₂ films revealed no carbon impurity incorporation from Hacac molecules (Figure S2e in the Supporting Information). These results confirm that the addition of Hacac (step A) to the WS₂ ALD process (steps B and C) does not influence the WS₂ deposition on a SiO₂ starting surface and on the WS₂ itself. Therefore, our process can be used to selectively deposit pure WS₂ (~2 monolayers) with angstrom-level thickness control on SiO₂ in the presence of Al₂O₃.

To quantify the selectivity of our process, we used the accepted definition of selectivity in the field of area-selective deposition:⁴⁵,⁴⁶

\[
\text{selectivity} = \frac{\theta_{GA} - \theta_{NGA}}{\theta_{GA} + \theta_{NGA}}
\]

where, \(\theta_{GA}\) and \(\theta_{NGA}\) represent the amount of material present (WS₂ in this case) on the growth and non-growth areas, respectively. Using this definition, the selectivity of the ABC-type WS₂ ALD process was calculated using the number of W XPS counts in Figure 2b. After 20 ALD cycles, a high selectivity value of ~0.95 was obtained. This corresponds to a selective deposition of WS₂ with a thickness of ~1 nm, which is more than one monolayer (one monolayer of WS₂ has a thickness of ~0.65 nm). After 30 cycles, the selectivity was determined to be ~0.82. This corresponds to a selective deposition of ~3 monolayers of WS₂. As the number of ALD cycles increases, the selectivity starts to decrease drastically (~0.45 after 50 ALD cycles). The loss in selectivity primarily arises from ineffective blocking of precursor adsorption by Hacac with increasing number of ALD cycles. A degraded blocking of the precursor adsorption can occur, because of the introduction of surface defects that influence Hacac adsorption negatively and/or incomplete Hacac coverage that allows the precursor molecules to access certain surface reactive sites.²³

To explore the versatility of our process on various surfaces, the ABC-type WS₂ ALD cycles were performed on several starting surfaces including TMDs and transition metal oxides, as shown in Figure 3. The integrated area of the XPS W 4p₃/₂ peaks on these surfaces were used to compare the ALD growth. The W 4p₃/₂ peaks were used to establish the nucleation curves in Figure 3 instead of the W 4f peaks as the W 4f peaks overlap with some of the elemental XPS peaks of the surface constituents (e.g., Hf 5p₃/₂ and Ti 3p₃/₂; see Figure S3 in the Supporting Information). Among various starting surfaces investigated, a growth delay of ~10 ALD cycles was observed on HfO₂ (Figure 3). Even after 50 ALD cycles, the integrated W 4p₃/₂ peak area was significantly lower on HfO₂ when compared to the peak area determined for a monolayer of WS₂ deposited on SiO₂ (dotted black line). The integrated W 4p₃/₂ peak area was observed to be also significantly lower on TiO₂. On the other hand, characteristic XPS W 4p₃/₂ peaks with relatively large integrated peak areas were observed on 2D TMDs including MoS₂, NbS₂, and TiS₂ starting surfaces, which indicated WS₂ film growth without any significant growth delay. As WS₂ grows readily on several TMD surfaces, our process can be also used to selectively grow 2D TMD vertical heterostructures (e.g., WS₂ on MoS₂) in the presence of the non-growth areas (i.e., Al₂O₃ and HfO₂). Immediate film growth was also observed on transition metal oxides such as MoO₃ and Nb₂O₅.

Raman spectroscopy is a widely used technique to establish and characterize the growth of crystalline TMD layers. Raman measurements revealed that our as-deposited AS-ALD WS₂ films on SiO₂ at 250 °C were amorphous in nature, because signature WS₂ Raman fingerprints were not observed. Cross-sectional TEM images (Figure S4a in the Supporting Information) indicated the growth of an amorphous WS₂ film matrix embedded with nanocrystalline regions. The growth mechanism for ALD MX₂ layers (both crystalline and amorphous) is not well understood in the literature. In our work, we believe that the growth mechanism for amorphous WS₂ layers is expected to occur similar to that of crystalline WS₂ layers with the exception of long-range ordering of the layers. A model for the WS₂ crystalline film growth during plasma-ALD is described in our previous works.⁴²,⁴⁷ The growth mode in amorphous WS₂ films (layer by layer or island growth, etc.) could vary, depending on the processing conditions and the defects present on the growth surface.

In order to improve the crystallinity of WS₂ layers, the samples were annealed at 450 °C in a H₂S gas atmosphere for 30 min in the same ALD reactor (pressure during annealing = 300 mTorr). WS₂ is considered to be a promising material for applications such as low-power devices in the back-end-of-line (BEOL).⁵ Therefore, the films were annealed within the thermal budget of BEOL-compatible processing (≤450°C). Upon annealing, signature Raman vibration modes for crystalline WS₂ were observed on SiO₂ (Figure 4b). The two characteristic Raman modes at 356 cm⁻¹ and 418 cm⁻¹ wavenumbers correspond to the WS₂ in-plane (\(E_{2g}\)) and out-of-plane (\(A_{1g}\)) vibrations.⁴⁸–⁵⁰ Cross-sectional TEM imaging (Figure S4b in the Supporting Information) showed a significant improvement in the crystallinity of the WS₂ layers upon annealing. The approximate grain size was ~10 nm, as deduced from top-view TEM (see Figures S4c and S4d in the Supporting Information). A detailed study on the fabrication and characterization of electronic devices such as field effect transistors (FETs), using the annealed WS₂ layers (including temperature-dependent resistivity measurements), will be performed in a separate study. The root-mean-square (rms)
surface roughness of the WS$_2$ films increased from $\sim$0.1 nm to $\sim$0.4 nm upon annealing, as determined from AFM measurements (Figure S5 in the Supporting Information). No Raman peaks were observed after performing WS$_2$ ABC cycles on Al$_2$O$_3$ as expected (see Figure 4b).

As a proof-of-concept, we tested our ABC-type AS-ALD process on patterned Al$_2$O$_3$/SiO$_2$ surfaces. ALD-grown Al$_2$O$_3$ was patterned on ALD-grown SiO$_2$ (Figure 4a), using a regular lift-off process. After performing 20 ALD cycles, the patterned samples were annealed at 450 °C in a H$_2$S atmosphere. Raman spectroscopy line scans were performed to investigate the selectivity over the patterned surfaces. The line scan of the $E'_{2g}$ Raman mode over the patterned surface revealed very clear and sharp transitions at the SiO$_2$/Al$_2$O$_3$ interfaces with steep slopes (Figure 4c).

XPS line scans were also performed on the annealed patterns to investigate the selectivity (see Figure S6 in the Supporting Information) for XPS W 4f core-level spectra. The XPS line scans in Figure 4d show strong W signals in the SiO$_2$ regions, whereas no W signals were observed in the Al$_2$O$_3$ regions. The overlap of the W and Al line scans at the interface can be attributed to the large spot size of the X-ray beam ($\sim$70 μm), which is comparable to the region of overlap and much larger than the spot size of the Raman laser ($\sim$5 μm).

In conclusion, we have demonstrated the area-selective deposition of 2D WS$_2$ nanolayers using ALD in a bottom-up processing approach. AS-ALD of WS$_2$ was achieved using acetylacetone (Hacac) inhibitor (A), bis(tert-butylimido)-bis(dimethylamido)-tungsten precursor (B), and H$_2$S plasma (C) pulses in an ABC-type ALD process at a low deposition temperature of 250 °C. With this approach, WS$_2$ nanolayers are readily deposited on SiO$_2$, various 2D TMDs and transition metal oxides, while growth on Al$_2$O$_3$ and HfO$_2$ surfaces is effectively blocked. On the growth areas, pure WS$_2$ is deposited with angstrom-level thickness control. The AS-ALD WS$_2$ films exhibited sharp Raman peaks, a fingerprint of crystalline film growth, upon annealing at BEOL-compatible temperatures ($\leq$450 °C). As a proof of concept, the AS-ALD process has been demonstrated on patterned Al$_2$O$_3$/SiO$_2$ surfaces. Raman line scans over the SiO$_2$/Al$_2$O$_3$ patterns showed very sharp peak intensity transitions at the interface. The selectivity of our process was quantified, and, after 20 ALD cycles (at least one monolayer), a high selectivity of 0.95 is obtained. The results obtained in this work can be used as a platform to further explore the area-selective deposition of other 2D TMD materials.

### EXPERIMENTAL PROCEDURES

All depositions were performed in a commercial FlexAL ALD reactor from Oxford Instruments. In essence, the reaction chamber is equipped with a remote inductively coupled plasma (ICP) source, a 200 mm substrate table, and a turbo molecular pump that enables a base pressure of $10^{-6}$ Torr. The reaction chamber wall temperature was set to 150 °C (maximum possible value), and the substrate table temperature was set to 250 °C. With these settings, the substrate temperature was estimated to be $\sim$200 °C, using a thermocouple on reference samples. The mismatch between the set and the estimate
temperature can arise from limited contact under vacuum. Table S1 in the Supporting Information compares the set temperature (referred to as deposition temperature) and estimated temperatures. Throughout this work, deposition temperatures are used for discussion. The WS₂ AS-ALD process was primarily tested and characterized on SiO₂ (growth area) and Al₂O₃ (non-growth area). Both SiO₂ and Al₂O₃ (∼30 nm) were deposited on c-Si with 450 nm thermal oxide using well-established ALD processes. Other starting surfaces reported in this work (various 2D TMDs and transition metal oxides) were also deposited using ALD processes. All substrates were subjected to a 20 min pre-heating step in a 200 mTorr Ar environment to stabilize the substrate temperature. The substrates were then subjected to a H₂ plasma for 5 min prior to the AS-ALD process. The H₂ plasma power was set to 500 W and the pressure in the chamber was maintained at 50 mTorr. The following optimized exposures were used in our PEALD recipe: 3 pulses of 5 s each for the Hacac dose (step A), 10 s for the bis(tert-butylimido)-bis(dimethylamido)-tungsten precursor dose (step B), and 60 s for the H₂S plasma exposure (step C). The Hacac inhibitor (Sigma–Aldrich, ≥99% purity) was stored in a canister at room temperature and was vapor-drawn into the reaction chamber. The two-step (BC) WS₂ PEALD recipe, employing the tungsten precursor and H₂S plasma pulses reported in our previous work, was used as a starting point to deposit WS₂ films. The growth inhibition on Al₂O₃ and thereby, the selectivity of our process was observed to be significantly dependent on ALD processing conditions including H₂S plasma exposure time, H₂ plasma pretreatment of Al₂O₃, and deposition temperature. This is further described in the Supporting Information (Figures S7 and S8). Frequent usage of H₂S plasma exposures beyond 60 s led to flaking of deposited material on the substrate table. Thus, H₂S plasma exposures were seemingly limited to 60 s during most of our processing.

In situ spectroscopic ellipsometry (SE) was used to measure the apparent WS₂ film thickness using a B-spline function or Cauchy-based parametrization to model the experimental SE data. All in situ SE measurements were performed using a J.A. Woollam Model M2000F ellipsometer. X-ray photoelectronic spectroscopy (XPS) was used to detect the presence of W on SiO₂ and Al₂O₃ surfaces. The XPS detection limit for W on top of SiO₂ and Al₂O₃ was determined to be below ∼0.01 monolayer (∼2 × 10¹² atoms/cm²). All XPS experiments were performed using a Thermo Scientific KA1066 spectrometer with monochromatic Al Kα X-ray source (hν = 1486.6 eV). The spot size of the incident X-rays was ∼70 μm. XPS data analysis was performed using the Avantage XPS software.

Scanning electron microscope (SEM) images were obtained using a Zeiss Sigma microscope with an in-column, secondary electron detector. The acceleration voltage of the electron beam was 2 keV. Raman spectroscopy was performed to investigate the characteristic vibrational modes in WS₂ films. Raman spectra were obtained using a Renishaw InVia Raman microscope equipped with a 514 nm laser at a power of ∼0.5 mW. The laser spot size was ∼5 μm. High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were obtained using a probe-corrected JEOL Model JEM-ARM200F transmission electron microscope (TEM) operated at 80 kV. For top-view STEM imaging, WS₂ layers were deposited on Si₃N₄ windows coated with 5 nm of ALD SiO₂. For cross-sectional TEM studies, WS₂ layers deposited on Si₃N₄ windows were coated with an additional SiO₂ protective layer on top. A focused ion beam was used to create a cross-sectional sample using the standard lift-out method. Atomic force microscopy (AFM) measurements were performed using a NT-MDT Solver P47 AFM system.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.0c00093.

Film growth on Al₂O₃, with and without Hacac; XPS data (W and S peak evolution and depth profiling of the C peak); overlap of XPS Ti and Hf peaks with W 4f peaks; TEM measurements: as-deposited and annealed WS₂; AFM measurements: as-deposited and annealed WS₂ XPS W 4f core-level spectra after annealing WS₂ sample; set temperature versus estimated substrate temperature; impact of processing conditions on the growth inhibition on Al₂O₃ surface (PDF)

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**Notes**
The authors declare no competing financial interest.

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