Conformal Growth of Nanometer-Thick Transition Metal Dichalcogenide TiS_x-NbS_x Heterostructures over 3D Substrates by Atomic Layer Deposition: Implications for Device Fabrication

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Abstract

The scalable and conformal synthesis of two-dimensional (2D) transition metal dichalcogenide (TMDC) heterostructures is a persisting challenge for their implementation in next-generation devices. In this work, we report on the synthesis of nanometer-thick 2D TMDC heterostructures...
consisting of TiSₓ-NbSₓ on both planar and 3D structures using atomic layer deposition (ALD) at low temperatures (200-300 °C). To this end, a process was developed for the growth of 2D NbSₓ by thermal ALD using (tert-butylimido)-tris-(diethylamino)-niobium (TBTDEN) and H₂S gas. This process complemented the TiSₓ thermal ALD process for the growth of 2D TiSₓ-NbSₓ heterostructures. Precise thickness control of the individual TMDC material layers was demonstrated by fabricating multilayer (5-layer) TiSₓ-NbSₓ heterostructures with independently varied layer thicknesses. The heterostructures were successfully deposited on large area planar substrates as well as over a 3D nanowire array for demonstrating the scalability and conformality of the heterostructure growth process. The current study demonstrates the advantages of ALD for the scalable synthesis of 2D heterostructures conformally over a 3D substrate with precise thickness control of the individual material layers at low temperatures. This makes the application of 2D TMDC heterostructures for nanoelectronics promising in both BEOL and FEOL containing high aspect ratio 3D structures.

Keywords: ALD, transition metal dichalcogenides, titanium disulfide, niobium disulfide, thin-films, heterostructure, conformality

**Introduction**

Layered two-dimensional (2D) transition metal dichalcogenides (TMDCs) such as MoS₂, NbS₂, etc., have attracted much interest for their unique electrical, optical, and mechanical properties. Lately, fabrication of nanometer-thick vertical heterostructures based on 2D TMDCs (e.g. WS₂-NbS₂) has gained significance over the formation of heterostructures based on 3D materials due to advantages such as absence of dangling bonds and lattice mismatch at the layers’ interface. Additionally, stacking different 2D materials on top of each other continues to open up unique functionalities which in turn leads to prospects for new application in various fields. For example: in 2D material based FETs (field effect transistors), 2D-2D
heterostructures provide superior device performance due to weak Fermi level pinning at the metal-semiconductor interface along with reduced Schottky barrier height compared to 2D-3D heterostructures\textsuperscript{10,11}. While 2D-2D TMDC vertical heterostructures exhibit large potential, the ability to fabricate them in nanometer-thickness on the wafer-scale (over large area) is a persisting challenge.

The most common fabrication technique for 2D heterostructures is a top-down approach known as the mechanical transfer method. In this method, the scotch tape technique is used to exfoliate 2D TMDC layers before aligning and placing them on top of another 2D TMDC layer to form the heterostructure. This approach provides significant flexibility to create various 2D heterostructure combinations\textsuperscript{12,3}. However, it is not a industrially scalable method and it has some important issues such as reproducibility, yield, and residue/contamination\textsuperscript{9}. Recently, chemical vapor deposition (CVD) has been explored as an alternative approach as a direct, bottom-up heterostructure synthesis method. In this method, a nanometer-thick CVD grown 2D TMDC is used as a substrate for the CVD growth of a second nanometer-thick 2D TMDC material. While, this method overcomes most of the above-mentioned limitations for 2D heterostructure synthesis\textsuperscript{13,14}, limitations such as large area uniformity (due to island growth leading to discontinuous films), nanometer thickness control, and high synthesis temperatures persist\textsuperscript{15}.

On top of the aforementioned constraints, capability to grow nanometer-thick 2D TMDCs heterostructures conformally on a 3D structure (including high aspect ratio) have yet to be explored using above mentioned methods. However, incompetency to grow conformally could be an additional bottleneck for implementation as the down-scaling of device dimensions continues with increasing level of structural complexity. Conformal growth means having complete coverage with uniform thickness of nanometer scale over a 3D structure. Control in growth of 2D TMDCs over complex 3D structures could also open new unique application
potential

potentials. For example: conformal growth of nanometer-thick 2D TMDCs as a copper metal-dielectric barrier layer in the back-end of the line (BEOL)\textsuperscript{16}. Furthermore, in the front-end of the line (FEOL), the ability to grow gate oxide and gate metal conformally around the channel in gate-all-around transistors (GAAFETs) makes continuous down-scaling of device dimensions below 5nm feasible\textsuperscript{17}. For further down-scaling the technology node below 5 nm or so, 2D TMDCs have emerged as strong contenders to overcome device performance limitations accompanied with down-scaling\textsuperscript{18}. Similar to GAAFETs, conformal growth of TMDCs and their heterostructures could thus be an added benefit in the fabrication of 2D based transistors (vdWFETs)\textsuperscript{19}. Therefore, conformality could be a valuable addition to the toolbox for 2D vertical heterostructure formation to fast track the implementation of 2D materials in nanoelectronic device process flows.

Lately, atomic layer deposition (ALD) has become of significance for the synthesis of various 2D TMDCs\textsuperscript{20,21–23}. It is a method which is based on self-limiting, saturated surface reactions where precursors are dosed in a cyclic manner, separated by purge steps to avoid parasitic CVD reactions\textsuperscript{24,25}. Due to its self-limiting nature, ALD provides precise Angstrom-level thickness control over a large area along with uniformity and conformality on complex 3D substrates at low processing temperatures. These attributes of ALD would be favorable for the fabrication of 2D TMDC heterostructures, as they can overcome the limitations observed in the aforementioned synthesis methods. Thus far, direct ALD of vertical heterostructures (i.e. layers of different materials stacked on top of each other) based on non-TMDC based layered materials such as Sb\textsubscript{2}Se\textsubscript{3}, Sb\textsubscript{2}Te\textsubscript{3} etc. have been successfully demonstrated over a large planar substrate\textsuperscript{26–28}. With reference to layered TMDC based heterostructure formation using ALD, there have been reports only on growing TMDCs on an exfoliated or CVD-grown TMDC substrate\textsuperscript{23,29}. On that account, to the best of our knowledge, direct synthesis of nanometer-thick 2D heterostructures based on layered TMDCs by ALD has not been demonstrated.
In this work, we report on a newly developed ALD process for niobium sulfide (NbS$_x$) growth, in addition to the previously reported process for titanium sulfide (TiS$_x$) film growth\textsuperscript{30}. Using these ALD processes, we synthesize nanometer-thick TMDC-TMDC vertical heterostructures in the form of TiS$_x$-NbS$_x$ heterostructures at low deposition temperatures (≤ 300 °C). Through deposition of multilayer (5 layers) TiS$_x$-NbS$_x$ heterostructures composed of TiS$_x$ and NbS$_x$ as the alternating layers with varying number of ALD cycles per individual layer, we demonstrate nanometer-thickness control of the individual material layers in the heterostructure. In addition to TMDC heterostructure formation on a planar substrate, we also demonstrate the conformal growth of multilayer nanometer-thick TiS$_x$-NbS$_x$ heterostructures on a 3D substrate consisting of a nanowire array. Our work shows that ALD is an excellent method to grow TMDC-TMDC vertical heterostructures over a large area with precise thickness control and conformality at low deposition temperatures.

**Experimental Details**

a) Atomic Layer Deposition

The TiS$_x$ and NbS$_x$ thin films were deposited by atomic layer deposition (ALD) using an Oxford Instruments Plasma Technology FlexAL ALD reactor. The base pressure of the system was 10$^{-6}$ Torr. The reactor acted as a hot wall reactor for depositions up to and including 150 °C, however, the reactor acted as a warm wall reactor for depositions above 150 °C as the wall temperature was maintained at 150 °C while the table temperature was varied between 150 °C and 450 °C. The metal-organic precursors tetrakis-(dimethylamido)-titanium (TDMAT) (Sigma-Aldrich Chemie BV, 99.999 %) and (tert-butylimido)-tris-(diethylamino)-niobium (TBTDEN) (STREM Chemical, Inc., 98%) were used for TiS$_x$ and NbS$_x$ growth, respectively. The TDMAT and TBTDEN precursors were kept in stainless steel bubblers at 50 °C and 65 °C, respectively and were bubbled using Ar as the carrier gas. In both ALD processes, the pressure
was maintained at 80 mTorr during both the precursor and coreactant exposure steps. In both the processes, the coreactant gas mixture consisted of 10 sccm of H₂S gas (>99.98 %) and 40 sccm of Ar gas (>99.999 %), respectively.

The TiSₓ process consists of the TDMAT precursor and the coreactant gas exposure for 4 s and 30 s, respectively. In the case of the NbSₓ process, the TBTDEN precursor exposure was 10 s, while the coreactant was dosed for 20 s. More details on ALD process optimization and saturation data for both processes are provided in Figure S1. In all cases, the precursor and coreactant exposure step were separated by Ar purge steps. The details about the TiSₓ-NbSₓ heterostructure formation such as deposition temperature and growth will be addressed in the results and discussion section. The thin films were deposited on Si substrates covered with approximately 450 nm thick thermally grown SiO₂ (planar substrate). The conformal growth studies were performed by growing the TiSₓ-NbSₓ heterostructures on an ALD SiO₂ coated regular array (pitch: 2 µm) of 2 µm long GaAs nanowires with a diameter of 60 nm thick (3D substrate).

b) Characterization Techniques

Scanning electron microscopy (SEM) was employed to investigate the surface morphology of the films. A Zeiss Sigma SEM with an in-lens detector and operating at an accelerating voltage of 3 kV was used for SEM studies. The microstructures of the thin film and the heterostructures were studied using (scanning) transmission electron microscopy [(S)TEM] with a JEOL ARM 200F microscope operated at 200 kV. For cross-section (S)TEM studies on planar Si substrates, a lamella (~100 nm) was prepared in a FEI Nova600i NanoLab SEM/FIB using the lift-out preparation procedure after a protective SiO₂ layer was deposited on the top of the film by electron-beam induced deposition (EBID). High-angle annular dark-field STEM (HAADF-STEM) combined with energy-dispersive X-ray spectroscopy (EDX) were used to
study the chemical composition of the TiS$_x$-NbS$_x$ heterostructures on both the planar Si and 3D nanowire substrates. The growth of the TiS$_x$ and NbS$_x$ thin films was investigated using in-situ spectroscopic ellipsometry (SE) where the film thickness was measured as a function of the number of ALD cycles. Data were collected every 10 ALD cycles by a J.A. Woollam Co., Inc., M2000U spectroscopic ellipsometer with a photon energy range of 0.7-5 eV. The dielectric function of the films was modeled using a B-spline model. The crystallinity of the thin films was studied by Gonio and grazing-incidence X-ray diffraction (XRD) with a PANalytical X’Pert Pro MRD analyzer using a Cu Kα ($\lambda = 1.54$ Å) X-ray source operated at 40 mA and 45kV. The scan range was 5 to 80° 2θ with a scan rate and step size of 0.2 s/step and 0.01, respectively. The composition and purity of the thin films were determined using Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) by Detect 99 B.V. Eindhoven, The Netherlands using a 2 MeV He$^+$ beam source and with the detectors at scattering angles of 105° and 170° for RBS, and 25° for ERD. X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific KA1066 spectrometer with monochromatic Al Kα ($hv = 1486.6$ eV) X-ray radiation to determine the binding environment and valence band spectra for the deposited thin films. Resistivity measurements were performed ex-situ at ambient conditions using a Signatone Four-Point Probe method in combination with a Keithley 2400 sourcemeter acting both as the current source and voltmeter. The resistivity of the thin films was determined from the slope of the obtained $I$-$V$ curves.

**Results and Discussion**

The film growth of both TiS$_x$ and NbS$_x$ by ALD was investigated independently before the synthesis of the TMDC-TMDC heterostructures based on TiS$_x$-NbS$_x$ was attempted. Thermal ALD processes for TiS$_x$ and NbS$_x$ were preferred over plasma-enhanced ALD processes for 2D TMDs, as plasma could cause interface mixing or damage during heterostructure
formation. In addition, thermal ALD processes could provide better conformal growth than plasma-enhanced ALD processes. We previously reported a thermal ALD process for TiS$_x$ films using TDMAT as precursor and H$_2$S gas as the coreactant. A thermal ALD process for NbS$_x$ films was developed in this work, using TBTDEN as the precursor and H$_2$S gas as the coreactant for deposition temperatures between 150 and 300 °C. More details on the NbS$_x$ ALD process optimization and film properties as a function of the deposition temperature can be found in the supporting information (Figure S1 and S2).

Next, to achieve high quality TiS$_x$-NbS$_x$ heterostructures, we investigated the properties of the individual TMDCs as a function of the deposition temperatures to determine the optimal deposition temperature. In the case of TiS$_x$, the film deposited at 200 °C had best crystallinity (see Figure 1a and S3). Cross-section HAADF-STEM analysis of TiS$_x$ deposited at 200 °C shows (Figure 1b) the layered 2D nature of the TiS$_x$ film. All van der Waals layers are oriented parallel to the substrate without any out-of-plane oriented (OoPO) growth. The average distance between the two layers was measured to be ~5.7 Å which is in good agreement with the distance between two layers of 1T-TiS$_2$. Likewise, the top-view SEM and cross-section STEM in Figure 1(a & c), respectively of the TiS$_x$ film deposited at 200 °C shows a smooth surface morphology with the absence of OoPO structures. The resistivity of the TiS$_x$ prepared at 200° C was measured to be below 0.8 mΩ-cm (see Table S1). This resistivity value is similar to the reported bulk resistivity of TiS$_2$.

NbS$_x$ films deposited at the highest temperature (at 300 °C) were observed to have the best crystallinity (see Figure S3). Yet, the crystallinity of the TiS$_x$ film grown at 200 °C is more pronounced than that of the NbS$_x$ film synthesized at 300 °C (see Figure 1g). The cross-section HAADF-STEM image of NbS$_x$ (Figure 1f) confirms these XRD results. The layer is polycrystalline, exhibiting a grain size of only a few nm’s and random grain orientation. As a result, the layered 2D nature was only visible in selected regions. The average distance between
two van der Waals layers was measured to be ~5.9 Å which is in accordance with the interlayer spacing value reported in the literature for NbS$_2$. The top-view SEM of the NbS$_x$ film (see Figure 1e and S4) shows that irrespective of deposition temperatures OoPO structures were present on the film surface. The density of OoPO structures decreased with increasing deposition temperature which led to relatively smooth surfaces for films deposited at 300 °C. Few of these OoPO structures were marked by white dotted circles in Figure 1e. Likewise, the cross-section HAADF-STEM image of the top part of the NbS$_x$ film in Figure 1d confirms the relatively smooth surface with few vertically tapered OoPO structures as highlighted by white dotted lines (also check Figure S5). The resistivity value of the NbS$_x$ deposited at 300°C was 4.8 mΩ·cm and is close to the reported bulk resistivity of NbS$_2$.

Figure 1 Top-view SEM images of ~30 nm thick TiS$_x$ (a) and NbS$_x$ (e) films deposited at 200 °C and 300 °C, respectively, on SiO$_2$/Si substrate. Cross-section HAADF-STEM image of the TiS$_x$ (b, c) and NbS$_x$ (d, f) films deposited at 200 °C and 300 °C, respectively. Note: (b, f) show cross-section views of the central part of the films while (c, d) show cross-section views of the surface of the films. (g) GI-XRD pattern of TiS$_x$ and NbS$_x$ films deposited at 200 °C and 300 °C, respectively. The dotted lines indicate the peak position corresponding to (001) and (003) planes of TiS$_x$ (blue) and NbS$_x$ (black), respectively.

a) Heterostructure Growth on a Planar Substrate
As ALD is a self-limiting cyclic process, the thickness of the film/layer can be controlled precisely by the number of ALD cycles. Linear growth in terms of film thickness as a function of the number of ALD cycles was observed for the TiS\textsubscript{x} and NbS\textsubscript{x} thermal ALD processes at 200 °C and 300 °C, respectively (see Figure S1c). The corresponding growth per cycle (GPC) values were measured (by taking the slope over the linear region of the curve) to be ~0.6 Å and ~1.17 Å, using in-situ SE measurements (Figure S1). It is important to note that TiS\textsubscript{x} could not be deposited above 200 °C due to decomposition of the TDMAT precursor above 200 °C. On the other hand, to obtain a good interface between TiS\textsubscript{x} and NbS\textsubscript{x} layers, growth of OoPO structures in NbS\textsubscript{x} needs to be avoided by depositing the film at 300 °C. Therefore, as schematically illustrated in Figure 2, two different deposition temperatures were used to grow TiS\textsubscript{x} (200 °C) and NbS\textsubscript{x} (300 °C) layers, and the table temperature was increased and decreased accordingly for the TiS\textsubscript{x}-NbS\textsubscript{x} heterostructure formation to acquire the best individual layer quality. Also note that TiS\textsubscript{x} growth on NbS\textsubscript{x} layers (and vice versa) using the above optimized thermal ALD processes were confirmed to be self-limiting in nature.

**Figure 2** Schematic illustration of the synthesis of the TiS\textsubscript{x}-NbS\textsubscript{x} heterostructure by thermal ALD. The TDMAT and TBTDEN correspond to Ti and Nb precursors, respectively.

In addition, to demonstrate thickness controllability by ALD, a 5-layer TiS\textsubscript{x}-NbS\textsubscript{x} heterostructure with varying individual layer thickness was fabricated (employing a process indicated by the grey dotted line in Figure 2). At 200 °C, ~15.0 nm of TiS\textsubscript{x} was deposited as
the first layer in the heterostructure using 260 cycles of TiS\textsubscript{x} thermal ALD process. On top of this TiS\textsubscript{x} layer, a NbS\textsubscript{x} layer was then deposited for 60 cycles at 300 °C. The 60 ALD cycles of NbS\textsubscript{x} would lead to a nominal thickness of ~5.8 nm (measured using \textit{in-situ} SE) on a SiO\textsubscript{2} as the starting surface, see Figure S1. However, the thickness of 60 cycles of NbS\textsubscript{x} ALD on TiS\textsubscript{x} as the starting surface might deviate from 5.8 nm due to possible differences in nucleation behavior. Therefore, from now on we use the term nominal thickness, which refers to the thickness of the material (for both TiS\textsubscript{x} and NbS\textsubscript{x}) when deposited for a N number of ALD cycles on SiO\textsubscript{2} as the starting surface. The buildup of the heterostructure continued with the deposition of layers comprised of TiS\textsubscript{x} (90 cycles), NbS\textsubscript{x} (60 cycles), and TiS\textsubscript{x} (180 cycles) with nominal thicknesses of ~5.1, ~5.8 nm, and ~10.7 nm, respectively. Both NbS\textsubscript{x} layers were limited to 60 ALD cycles to minimize the appearance of OoPO structures (marked by white circles in Figure 1c) at the interface. Additionally, during heating and cooling of the substrate table between 200 °C and 300 °C for the growth of TiS\textsubscript{x} and NbS\textsubscript{x} layers repectively, the sample was transferred to the load lock chamber from the ALD chamber to reduce annealing effects at the elevated temperatures. While the number of layers in the heterostructure was restricted to five in this work, this process can be easily repeated by any number of times to grow multilayer heterostructures with varied individual layer thickness.

The microstructure of the synthesized 5-layer TiS\textsubscript{x}-NbS\textsubscript{x} heterostructure was then studied by cross-section (S)TEM imaging as shown in Figure 3. A clear difference in contrast can be observed between the TiS\textsubscript{x} and NbS\textsubscript{x} layers in bright field TEM (Figure 3a), due to the difference in mass density between the materials: the TiS\textsubscript{x} layers appear bright, while the NbS\textsubscript{x} layers are dark. Furthermore, considering the width of the lamella being ~100 nm, the sharp transition in layer contrast between the TiS\textsubscript{x} (light) and NbS\textsubscript{x} (dark) layers in the TEM image indicates a sharp interface between the layers, with low degree of mixing. The average vertical thickness of each individual layer was measured by taking an average of thickness
measurements from several cross-section HAADF-STEM images. The measured layer thickness of the three TiS\textsubscript{x} layers (layer 1, 3 and 5) were \(14.4\pm0.9\), \(4.9\pm0.5\) and \(10.2\pm0.6\) nm, respectively, and that of the two NbS\textsubscript{x} layers (layer 2 and 4) were \(4.2\pm0.6\) and \(4.5\pm0.4\) nm, respectively.

The measured thickness of both the TiS\textsubscript{x} (layer 3 and 5) layers grown on NbS\textsubscript{x} as the starting surface were comparable to the expected nominal thickness of 5.1 and 10.7 nm, respectively. On the contrary, the measured thickness of both NbS\textsubscript{x} (layer 2 and 4) layers grown on TiS\textsubscript{x} as the starting surface was lower than the nominal thickness of 5.8 nm. The lower than expected thickness in the case of NbS\textsubscript{x} could be due to nucleation delay on the TiS\textsubscript{x} starting surface in comparison to a SiO\textsubscript{2} starting surface. This change in growth indicates the higher sensitivity of the NbS\textsubscript{x} thermal ALD process to the starting surface chemistry over the TiS\textsubscript{x} thermal ALD process. Similar nucleation delays have also been observed for several other ALD processes, as ALD critically depends on the starting surface chemistry\textsuperscript{36,37}.

Differences in crystallinity between the TiS\textsubscript{x} and NbS\textsubscript{x} layers can also be observed in Figure 3a. Here the TiS\textsubscript{x} layers display the expected layered structure with clearly visible van der Waals gaps, while the NbS\textsubscript{x} layers lack significant ordering and appear much more amorphous. This is in agreement with the observations from GI-XRD and STEM in Figure 1 for the individual TiS\textsubscript{x} and NbS\textsubscript{x} films of 30 nm each. The intensity of the 15° 20 peak (corresponding to the (001) and (003) planes for both TiS\textsubscript{2} and NbS\textsubscript{2}, respectively) in the XRD spectrum was observed to be much stronger for the TiS\textsubscript{x} film than for the NbS\textsubscript{x} film indicating a higher crystallinity. This shows that the observed crystallinity differences between the TiS\textsubscript{x} and NbS\textsubscript{x} layers is intrinsic to the respective ALD processes and not due to growth in the heterostructure. Although the NbS\textsubscript{x} is lower in crystallinity, there are regions where a continuous layered van der Waals formation is clearly visible through all five layers of the heterostructure. Therefore, provided NbS\textsubscript{x} layers were also synthesized with equally high crystallinity as TiS\textsubscript{x} layers, this
shows that ALD has the capability to synthesize high quality 2D van der Waals heterostructures with relatively sharp interfaces *in-situ* without exposing to ambient condition.

**Figure 3** (a) Cross-section bright-field TEM image of the TiS$_x$-NbS$_x$ heterostructure with 5 layers on the Si wafer with native SiO$_2$ on top. (b) Cross-section HAADF-STEM image of the
TiS\textsubscript{x}-NbS\textsubscript{x} heterostructure layers. (c-e) Corresponding EDX elemental mapping of Ti, Nb and S, respectively.

A HAADF-STEM image of the heterostructure is shown in Figure 3b, and the corresponding EDX elemental mapping of Ti, Nb and S are shown in Figure 3c-d, respectively. The EDX maps of both Ti and Nb confirm the presence of two NbS\textsubscript{x} layers of similar thickness, sandwiched between three TiS\textsubscript{x} layers of different individual layer thickness. The EDX mapping also reveals the lack of inter-mixing between the two elements per layer, as no Ti was observed in the NbS\textsubscript{x} layer within the detection limits of EDX. Likewise, no Nb counts were detected in the TiS\textsubscript{x} layers. Therefore, the EDX mapping strongly indicates that ALD can fabricate TMDC heterostructures with little interlayer mixing.

On the other hand, the S mapping shows a difference in S content between TiS\textsubscript{x} and NbS\textsubscript{x} layers, as S counts were observed to be relatively low in the NbS\textsubscript{x} layers. This could indicate differences in the chemical composition/stoichiometry between the TiS\textsubscript{x} and NbS\textsubscript{x} layers. Consequently, the chemical composition of both TiS\textsubscript{x} and NbS\textsubscript{x} films deposited at 200 °C and 300 °C, respectively were individually investigated using RBS, see Table S1. From the RBS measurements, the stoichiometry (sulfur to transition metal ratio) of both the films was calculated to be 1.41 and 1.25 for TiS\textsubscript{x} and NbS\textsubscript{x}, respectively. This confirms the difference in stoichiometry between the two films while also revealing relatively low S content, especially in the NbS\textsubscript{x} film. This indicates the presence of S vacancies and/or excess metal in both layers. In addition, RBS revealed the presence of 6-9 at.% of H, 7 at.% of C and 1 at.% of O impurities in both TiS\textsubscript{x} and NbS\textsubscript{x} ALD grown films, see Table S1. The detected H and C in the films could be from precursor ligands and/or coreactant. The observed O impurities in the film could be due to presences of residual O\textsubscript{2} and H\textsubscript{2}O in the background of the ALD chamber during deposition.
Figure 4 (a) Side-view HAADF-STEM image of the ALD SiO$_2$ coated GaAs nanowire, grown from a Au seed particle, covered with the TiS$_x$-NbS$_x$ heterostructure. (b-e) Higher magnification (red box in (a)) HAADF-STEM image and the corresponding EDX elemental mapping of Ti, Nb and S, respectively.

b) Heterostructure growth on a 3D substrate

Finally, to demonstrate conformality, an analogous 5-layer TiS$_x$-NbS$_x$ heterostructure was deposited on an array of wurtzite GaAs nanowires (3D substrates) which were coated with SiO$_2$ by ALD. The coverage of the 5-layer heterostructure on the nanowires was analyzed with side-view HAADF-STEM (Figure 4a) upon aligning the wurtzite GaAs nanowire to its $<$11-20$>$ zone axis, allowing for imaging parallel to the $<$10-10$>$ side facets. The HAADF-STEM image shows the complete coverage of the nanowire with the heterostructure over the length as well as the curvature (tip) of the nanowire (formed by the Au catalyst particle used for the nanowire growth), confirming conformal growth (Figure S6 shows the SEM image containing multiple nanowires). Furthermore, the thickness of the heterostructure was measured on various spots along the length of the nanowire and was observed to hardly vary, with a thickness variation of $<5\%$. Thus, this validates the uniform growth of the 5-layer heterostructure on a 3D structure.

Figure 4b shows the magnified STEM image of the nanowire (red box) and the corresponding EDX elemental mapping of Ti, Nb and S, respectively are shown in Figure 4(c-
The STEM image along with EDX maps confirms the synthesis of the 5-layer TiSₓ-NbSₓ heterostructure. The Ti mapping shows three TiSₓ layers with different individual layer thickness as expected. The Nb mapping shows two NbSₓ layers with comparable thickness sandwiched between TiSₓ layers. The average individual layer thicknesses were measured on various spots on the STEM image (Figure 4(b)) and it was observed that the TiSₓ layers grown on NbSₓ layers were measured to be 4.9 and 10.4 nm, respectively (layer 3 and 5). The thicknesses of the NbSₓ layers on top of the TiSₓ layers were measured to be 4.4 and 4.7 nm (layer 2 and 4), respectively. These values are comparable to the individual layer thickness observed on a planar Si wafer. Thus, confirms the precise thickness control of all five individual layers in the TiSₓ-NbSₓ heterostructure over the nanowire and the absence of intermixing between the layers. Hence, this strongly establishes the capability of ALD for the scalable synthesis of 2D TMDC vertical heterostructures with sharp interfaces, excellent uniform coverage and conformally over a 3D structure at low temperature.

**Conclusions**

In this work, ALD has been successfully applied as a suitable technique to synthesize nanometer-thick 2D TMDC vertical heterostructures. A TiSₓ-NbSₓ heterostructure consisting of 5-layers with different individual layer thickness was deposited on a planar Si wafer as well as on a 3D substrate. The thickness of the individual layers was controlled precisely by varying the number of ALD cycles of the corresponding thermal ALD process. We successfully demonstrated large area uniformity and conformality over a 3D substrate at low deposition temperatures. The ability to synthesize TMDC and their heterostructures by ALD with conformal growth over 3D structures at low temperatures could be beneficial to open fresh avenues such as fabricating complex 3D device structures (partly) consisting of 2D TMDCs both in BEOL and FEOL for nanoelectronics. Furthermore, the current work can be extended
to synthesize other 2D TMDC based heterostructures such as metal-semiconductor heterostructures.

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**Supporting Information**

Overview of thermal ALD process development and film characterization for NbS\textsubscript{x} and TiS\textsubscript{x} film growth as a function of deposition temperature, ALD saturation curves, thickness as a function of number of ALD cycles using SE, detailed analysis of XPS spectra, XPS: valence band spectra, DFT simulated valence band spectra for NbS\textsubscript{2}, RBS, film resistivity, crystallinity using XRD, and film morphology using SEM.
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Supporting Information

Conformal Growth of Nanometer-Thick Transition Metal Dichalcogenide TiS$_x$-NbS$_x$ Heterostructures over 3D Substrates by Atomic Layer Deposition: Implications for Device Fabrication

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TiS$_x$ and NbS$_x$ Film Growth by ALD

In this work, thin films of TiS$_x$ and NbS$_x$ were deposited by ALD on a thermally grown 450 nm SiO$_2$/Si substrate. Unless otherwise mentioned this was the standard starting substrate. The TiS$_x$ thermal ALD process used in this work was reported previously$^1$. For NbS$_x$ growth a new process was developed by thermal ALD using (tert-butylimido)-tris-(diethylamino)-niobium (TBTDEN) and H$_2$S gas as coreactant. The self-limiting saturated growth behavior for the NbS$_x$ ALD processes was investigated at 250 °C. All the growth-per-cycle (GPC) values were determined by measuring the thickness as a function of the ALD cycle measurement by \textit{in-situ} Spectroscopic Ellipsometry (SE). Saturation of the GPC was observed when at least 10 s and 20 s of TBTDEN precursor and H$_2$S coreactant gas were pulsed, respectively and when both were separated by a 30 s Ar purge steps to avoid parasitic CVD reactions (See Figures S1(a&b) (red)). The GPC value under saturated growth conditions was 1.65 Å.
For the TiSₓ thermal ALD process, the growth and film properties at deposition temperatures above 100 °C were not discussed in the previous work. Therefore, the growth behavior as a function of the deposition temperature was investigated for both ALD processes. For various deposition temperatures in both ALD processes, the thickness as a function of the number of ALD cycles was determined by *in-situ* SE as shown in Figure S1(c&d). The deposition temperatures were varied between 100 °C and 200 °C for the TiSₓ process, and between 150 °C and 300 °C for the NbSₓ process. Indicating a narrow temperature window for the combined processes, as TiSₓ film could not be deposited above 200 °C due to the decomposition of TDMAT, while in the case of the NbSₓ, film growth was not observed below 150 °C. In the case of TiSₓ, linear ALD growth was observed without any delay at all deposition temperatures, see Figure S1c. The GPC was calculated by taking a slope over above 50 cycles, and it was observed that the GPC decreases from 1.6 to 0.6 Å with increasing deposition temperature, see Table S1. On the contrary, for the NbSₓ case, below a deposition temperature of 300 °C, immediate nucleation up until 10 ALD cycles was observed. Following this initial nucleation there is a growth delay between 10 and ~80 cycles, see Figure S1d. This indicates that the initial nucleation on the SiO₂ substrate was rapid, and the further growth on deposited/nucleated NbSₓ layers was delayed significantly at lower deposition temperature (150 °C). However, by increasing the deposition temperature from 150 to 250 °C the delayed growth between 10 and ~80 cycles were observed to recover. Leading to increasing trend in GPC along with deposition temperature from 1.52 Å at 150 °C to 1.65 Å at 250 °C. On the contrary, the growth behavior at 300 °C was different, as linear ALD growth was observed without any trend of delayed growth. The GPC at 300 °C was measured to be 1.17 Å, which is lower than the GPC at 250 °C. This drop in GPC at 300 °C could be ascribed to changes in film morphology, as will be discussed later.
Figure S1 (a) and (b) Saturated curves for TiS$_x$ and NbS$_x$ as a function of precursor dose time and coreactant gas dose time, respectively. (c) and (d) Thickness as a function of the number of ALD cycles for both TiS$_x$ and NbS$_x$ processes, respectively for various deposition temperatures.

**Composition Analysis**

The TiS$_x$ and NbS$_x$ films deposited at various deposition temperatures were characterized in detail. The elemental composition of the deposited films was studied using XPS analysis. The S$_{2p}$ XPS spectra for both the TiS$_x$ and NbS$_x$ films deposited at various deposition temperatures are shown in Figure S2(a&b). All films were observed to have one doublet at ~161.1 and ~162.3 eV, corresponding to S 2p$_{3/2}$ and S 2p$_{1/2}$ spin-orbit doublets of S$^{2-}$ species in MX$_2$ type materials, indicating the disulfide (TiS$_2$ and NbS$_2$) nature of the films. Depth profiling of the films by means of sputtering using Ar$^+$ ions was performed to study the purity of the films at the bulk by avoiding surface oxidation/impurities due to exposure to ambient condition. The depth
profiling revealed the presence of C, O, and N impurities. Further, to avoid the influence of preferential sputtering on the qualitative composition of these impurities and to obtain the chemical composition of the film, RBS studies were performed on these films, as shown in Table S1.

To further confirm the synthesis of TiS\textsubscript{x} and NbS\textsubscript{x}, valence band spectra were measured using XPS, see Figure S2. The valence band spectra of the TiS\textsubscript{x} films deposited at various temperatures are in good agreement with the TiS\textsubscript{2} valence band spectra reported in the literature\textsuperscript{2}. Additionally, an evolution of a shoulder close to the Fermi level around \(~\)\textasciitilde\textasciitilde1 eV (marked with *) was observed and the intensity of this peak increased with increasing deposition temperature. Similarly, in literature, Hawkins \textit{et. al.} using UPS valence band spectra measurements, observed a peak around -1 eV, and they attribute this peak to Ti\textsuperscript{3\textchar'\textasciiacute} defect states in TiS\textsubscript{2}\textsuperscript{3}. Following the literature, the observed peak around -1 eV was also attributed to Ti\textsuperscript{3\textchar'\textasciiacute} (and/or Ti\textsuperscript{2\textchar'\textasciiacute}) defect states indicating the presence of S vacancies and/or excess Ti in the TiS\textsubscript{x} films\textsuperscript{4}. In the case of NbS\textsubscript{x} films, we could not find any literature on the valence band spectra NbS\textsubscript{2}, therefore, the spectrum was simulated for the NbS\textsubscript{2} crystal structure\textsuperscript{5} using density functional theory (DFT), see Figure S2e. This simulated spectrum was compared with the measured spectra and yields a good match with the spectra indicating the synthesis of NbS\textsubscript{2} films. Similar to the TiS\textsubscript{x} case, the shoulder close to the Fermi level around \(~\)\textasciitilde\textasciitilde1 eV (an intrinsic NbS\textsubscript{2} valence band spectrum peak) in the valence band spectra of NbS\textsubscript{x} film was observed to increase in peak intensity with increasing deposition temperatures. This peak could also be attributed to Nb\textsuperscript{3\textchar'\textasciiacute} (and/or Nb\textsuperscript{2\textchar'\textasciiacute}) defect states indicating the presence of S vacancies and/or excess Nb in the NbS\textsubscript{x} films.
Figure S2 (a) and (b) XPS S2p spectra of TiS$_x$ and NbS$_x$ films, respectively for various deposition temperatures. (c) and (d) shows the XPS valence band spectra of TiS$_x$ and NbS$_x$ films, respectively for various deposition temperatures. In (c) grey area marked with ‘*’ indicates defect states in TiS$_2$. (e) DFT simulated valence band spectra using the crystal structure parameters of NbS$_2$. 
Table S1: Growth and material properties of the TiS\textsubscript{x} and NbS\textsubscript{x} film, such as GPC, resistivity, H, C, and O content, and S/transition metal ratio for various deposition temperatures. The GPC was calculated using the \textit{in-situ} SE measurement as a function of the number of ALD cycles. Resistivity was calculated using the Four-Point Probe measurements. The H, C, O at.% and S/transition metal ratio were obtained from RBS and ERD measurements.

| TiS\textsubscript{x} | GPC (Å) | Resistivity (10\textsuperscript{3} μΩ-cm) | H (at.%) | C (at.%) | O (at.%) | S/Ti ratio |
|----------------------|---------|---------------------------------|--------|--------|--------|------------|
| 100 °C               | 1.60 ± 0.03 | 2.4 ± 0.1         | 18.8 ± 0.4 | 5.6 ± 1.2 | 4.2 ± 1.6 | 1.8 ± 0.1  |
| 150 °C               | 0.72 ± 0.03 | 1.2 ± 0.1         | 10.8 ± 0.7 | 1.1 ± 0.1 | 6.7 ± 0.1 | 1.5 ± 0.1  |
| 200 °C               | 0.60 ± 0.03 | 0.8 ± 0.1         | 6.3 ± 0.5  | x       | 7.1 ± 0.1 | 1.4 ± 0.1  |

| NbS\textsubscript{x} | GPC (Å) | Resistivity (10\textsuperscript{3} μΩ-cm) | H (at.%) | C (at.%) | O (at.%) | S/Nb ratio |
|----------------------|---------|---------------------------------|--------|--------|--------|------------|
| 150 °C               | 1.52 ± 0.03 | 16.4 ± 0.1        | -      | -      | -      | -          |
| 200 °C               | 1.54 ± 0.03 | 12.8 ± 0.1        | 23.7 ± 1.5 | x      | 5.6 ± 0.2 | 1.5 ± 0.1  |
| 250 °C               | 1.65 ± 0.03 | 8.6 ± 0.1         | -      | -      | -      | -          |
| 300 °C               | 1.17 ± 0.03 | 4.8 ± 0.1         | 9.2 ± 0.7  | x      | 7.5 ± 0.3 | 1.3 ± 0.1  |

“\_\_” no data
“x” below detection limit

To expand on XPS analysis and to obtain an in-depth understanding of the composition of both the TiS\textsubscript{x} and NbS\textsubscript{x} films as a function of deposition temperature RBS study was performed. For both TiS\textsubscript{x} and NbS\textsubscript{x} films, S to transition metal (Ti or Nb) ratio was calculated from RBS measurements. RBS revealed substoichiometry for both the material systems with a value less than 2, and the ratio was observed to decreases with increasing deposition temperatures. In the case of TiS\textsubscript{x} film, the ratio decreased from 1.75 for 100 °C to 1.41 for 200 °C film. Whereas, in the case of NbS\textsubscript{x} films, the ratio decreased from 1.47 for 200 °C to 1.25 for 300 °C film. This indicates the presence of S vacancies and/or excess metal in the films, similar to the observation made by XPS valence band measurement. In addition to the S to transition metal ratio, there were also other similarities in case of impurities between TiS\textsubscript{x} and NbS\textsubscript{x} ALD grown films. Note that the substoichiometric nature of the films could explain the absence of Raman signals for both TiS\textsubscript{x} and NbS\textsubscript{x} films. The H content decreases in both cases (Table S1) with increasing...
deposition temperatures from ~18 to 6 at.% for TiS\textsubscript{x} films, and from ~23 to 9 at.% for NbS\textsubscript{x} films. The presence of H in the film could be from precursor ligands and/or coreactant. The C content for TiS\textsubscript{x} films decreases from ~5 at.% at 100 °C to below detection limit at 200 °C, while for NbS\textsubscript{x} films, it was below the detection limit irrespective of deposition temperatures. The C content in the film could be from precursor ligands. Whereas, O content increases for both the processes with increasing deposition temperature from ~4 to 7 at.%., and could be due to residual O\textsubscript{2} and H\textsubscript{2}O present in the ALD reactor during deposition.

**Crystallinity and Morphology Analysis**

The role of deposition temperature on the crystallinity and the film morphology of both films was investigated using XRD and SEM analysis, respectively. The XRD patterns of both the TiS\textsubscript{x} and NbS\textsubscript{x} films are shown in Figure S3, where the crystallinity of the films was observed to increase with increasing deposition temperature. Both the GI-XRD and gonio-XRD (shown in the inset of the Figure S3a) patterns of the TiS\textsubscript{x} films indicate that the crystallinity increases significantly with increasing deposition temperature. The only peak visible in both the scan was around 15° 2θ, which corresponds to the (001) plane of the 1T phase of TiS\textsubscript{2}. The gonio-XRD shows that the basal (001) plane growth of the TiS\textsubscript{x} film increases with increasing temperature. Similarly, the crystallinity of the NbS\textsubscript{x} films also increases with deposition temperature. The peak around 15° 20 appears and increases in intensity for the films deposited at higher temperatures, and this peak corresponds to the (003) plane of the NbS\textsubscript{2}. The gonio XRD (data not shown here) did not show any peaks confirming the poor crystallinity of the NbS\textsubscript{x} films. Therefore, note that the relative crystallinity of the 300 °C NbS\textsubscript{x} film was poor in comparison to the TiS\textsubscript{x} film deposited at 200 °C. The broad peak around 20° 20 for the films at all deposition temperatures also indicates the amorphous content in the films.
Figure S3 (a) and (b) GI-XRD patterns for TiSₓ and NbSₓ films, respectively, deposited at various deposition temperatures. Inset in (a) shows the Gonio XRD pattern for TiSₓ films deposited at various deposition temperatures.

The top-view SEM image of TiSₓ film deposited at 100°C (Figure S4a), shows out-of-plane orientation (OoPO) structures also known as fins. Similar OoPO structures were also observed for TiS₂ films deposited by PE-ALD¹, and also for other TMDCs synthesized by ALD such as MoS₂⁶, and ReS₂⁷. The number of OoPO structures was observed to decrease with increasing deposition temperature. At 200 °C (see Figure S5c) OoPO structures were not observed. In the case of NbSₓ films, the top-view SEM images show OoPO structures for all deposition temperatures, see Figure S4(e-f). For the films deposited between 150 and 250 °C, a high density of OoPO structures was observed, while at 300 °C the OoPO structures were observed to be suppressed. This significant change in morphology from 250 °C to 300 °C, can also explain the change in growth behavior observed in Figure S1d. A similar effect of the OoPO structure on GPC has been observed previously for PE-ALD grown TiS₂¹ and MoS₂⁶, where the GPC was observed to rise due to the OoPO structures of the film. Therefore, the suppression of the OoPO structures could explain the decreasing GPC at 300 °C for the NbSₓ process.
Figure S4 Top-view SEM image of deposited TiS\(_x\) (a-c) and NbS\(_x\) (e-h) films at various deposition temperatures. (d) shows the cross-section STEM image of the TiS\(_x\) film deposited at 200 °C.

**Resistivity measurements**

The resistivity of the films was calculated using Four-Point Probe measurements for both TiS\(_x\) and NbS\(_x\) films deposited at different deposition temperatures, see Table S1. It was observed that the resistivity of both films decreases with increasing deposition temperature. The resistivity of TiS\(_x\) films decreases from 2.4 x10\(^3\) for 100 °C to 0.8 x10\(^3\) μΩ-cm for 200 °C film. And that of NbS\(_x\) films decreases from 16.4 x10\(^3\) for 150 °C to 4.8 x10\(^3\) μΩ-cm for 300 °C film. Such a variation in resistivity of the films could be due to one or more factors such as morphology, decreasing stoichiometry and/or increasing crystallinity of the films. In literature, the TiS\(_2\) resistivity has been observed to decrease with the sub-stoichiometric of the films\(^8,3,4\). Such a trend of a decreasing resistivity was reported to be due to an increasing number of defect states near the Fermi level with increasing level of sub-stoichiometry in the films. This could also explain the trend observed here for both TiS\(_x\) and NbS\(_x\) films as the presence of defect states near the Fermi level (XPS valence band spectra) increases with the sub-stoichiometry of the films, thus clearly indicating the role of stoichiometry in the films on resistivity. It is also important to note that in addition to film stoichiometry, film crystallinity plays an additional
role in the resistivity of the film, as metallic NbS$_x$ film with S/Nb ratio of 1.25 deposited at 300 °C has a higher resistivity than the TiS$_x$ film with S/Ti ratio of 1.41 deposited at 200 °C, considering that the bulk resistivity of both the TiS$_2$ and NbS$_2$ are roughly similar\cite{4,9}. The resistivity of the fabricated 5-layer TiS$_x$-NbS$_x$ heterostructure was measured to be 1 $10^3$μΩ·cm.

**OoPO structure in NbS$_x$**

![Cross-section HAADF-STEM image of NbS$_x$ deposited at 300 °C. The highlighted red box shows an OoPO structure in the NbS$_x$ film.](image)

**Figure S5** Cross-section HAADF-STEM image of NbS$_x$ deposited at 300 °C. The highlighted red box shows an OoPO structure in the NbS$_x$ film.
SEM image of Ti$_x$-Nb$_x$ heterostructure coated nanowire array

**Figure S6** Top-view (a) and 45°-view (b) SEM image of the ALD SiO$_2$ coated GaAs nanowire array, grown from a Au seed particle, covered with the 5-layer Ti$_x$-Nb$_x$ heterostructure.
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