Low-Temperature Phase-Controlled Synthesis of Titanium Di- and Tri-sulfide by Atomic Layer Deposition

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Supporting Information

ABSTRACT: Phase-controlled synthesis of two-dimensional (2D) transition-metal chalcogenides (TMCs) at low temperatures with a precise thickness control has to date been rarely reported. Here, we report on a process for the phase-controlled synthesis of TiS2 (metallic) and TiS3 (semiconducting) nanolayers by atomic layer deposition (ALD) with precise thickness control. The phase control has been obtained by carefully tuning the deposition temperature and coreactant composition during ALD. In all cases, characteristic self-limiting ALD growth behavior with a growth per cycle (GPC) of ~0.16 nm per cycle was observed. TiS2 was prepared at 100 °C using H2S gas as coreactant and was also observed using H2S plasma as a coreactant at growth temperatures between 150 and 200 °C. TiS3 was synthesized only at 100 °C using H2S plasma as the coreactant. The S2 species in the H2S plasma, as observed by optical emission spectroscopy, has been speculated to lead to the formation of the TiS3 phase at low temperatures. The control between the synthesis of TiS2 and TiS3 was elucidated by Raman spectroscopy, X-ray photoelectron spectroscopy, high-resolution electron microscopy, and Rutherford backscattering study. Electrical transport measurements showed the low resistive nature of ALD grown 2D-TiS2 (1T-phase). Postdeposition annealing of the TiS3 layers at 400 °C in a sulfur-rich atmosphere improved the crystallinity of the film and yielded photoluminescence at ~0.9 eV, indicating the semiconducting (direct band gap) nature of TiS3. The current study opens up a new ALD-based synthesis route for controlled, scalable growth of transition-metal di- and tri-chalcogenides at low temperatures.

I. INTRODUCTION

Since the isolation of monolayer graphene, two-dimensional (2D) materials such as the transition-metal di-chalcogenides (TMDCs) have shown interesting electrical and optical properties.1 TMDCs consist of a transition metal (such as Mo, W, Ti, Nb, etc.) paired with a chalcogenide (S, Se, and Te) forming a layered structure in which the layers are held together by weak van der Waals forces. Besides TMDCs, there is an alternative class of low-dimensional materials that consist of similar elements to TMDCs. This class of materials is known as the transition-metal tri-chalcogenides (TMTCs) and consists of quasi-one-dimensional materials possessing an added degree of freedom that results in a strong electrical and optical in-plane anisotropy.2,3 The TMTCs are known for the groups IV, V, and VI transition metals (such as Ti, Hf, Nb, etc.) and are predominantly semiconducting in nature. The electrical properties can vary between di- and tri-chalcogenide systems containing analogous elements. For example, TiS2 and NbS2 are considered a semimetal and metal, respectively, whereas TiS3 and NbS3 are both semiconductors. Therefore, controlling phase transitions between TMDCs and TMTCs during synthesis allows for direct tailoring of the electrical characteristics of these low-dimensional materials. This phase control could offer new possibilities for device fabrication.

Titanium sulfide (TiS2) is one of the systems that could provide an excellent framework for phase control during synthesis. TiS2 has been studied extensively for batteries,7 optics,8 and thermoelectric material applications and has been synthesized by various techniques such as chemical vapor transport (CVT),10 chemical vapor deposition (CVD),11−15 atomic layer deposition (ALD),16−18 and wet chemical synthesis.19 Interestingly, the electrical properties of TiS2 have been under debate for the last few decades, with hypotheses from both theory and experimental results splitting...
between a semiconducting, metallic, or semimetallic nature.\textsuperscript{20,21} Recently, TiS\textsubscript{2} has been considered as a degenerate, small-gap semiconductor or a semimetal owing to its high conductivity and optical absorption properties.\textsuperscript{22} Conversely, TiS\textsubscript{3} has a direct band gap in the infrared region (0.9−1 eV) irrespective of its thickness and is the only known TMTC possessing a direct band gap.\textsuperscript{3} This makes TiS\textsubscript{3} an ideal candidate for (opto)electronics applications.\textsuperscript{23,24} It is known from the literature that TiS\textsubscript{3} is less common to synthesize, with reports predominantly using CVT methods\textsuperscript{1} with a few instances of CVD.\textsuperscript{1,3,25,26} CVT is a technique where elemental Ti and S are sealed inside a quartz ampoule and placed inside a furnace for synthesis, making this a nonscalable (i.e., not wafer-scale), relatively high temperature, and time-consuming technique.\textsuperscript{3−5,27}

In TiS\textsubscript{2}, CVT synthesis\textsuperscript{10} phase control can be attained by carefully modulating both the S to Ti ratio and the process temperature. TiS\textsubscript{2} is obtained with an initial S to Ti ratio of 2, whereas TiS\textsubscript{3} is obtained by maintaining a S to Ti ratio above 3. Temperature is also important due to pyrolysis of S from TiS\textsubscript{2} above 550 °C. Thus, TiS\textsubscript{3} must be synthesized at or below 550 °C. A significant drawback of the CVT technique is that it requires days to weeks at high temperatures (>450 °C) for growing large crystals (>1 cm), which can be subsequently used to mechanically exfoliate 2D flakes of several microns in size. Thus, a technique to rapidly synthesize both TiS\textsubscript{2} and TiS\textsubscript{3} over a large area (wafer-scale) with high uniformity and with controlled thickness would be very beneficial for nanoelectronic applications.

In this work, using atomic layer deposition (ALD) as a synthesis technique, we address the challenges associated with other synthesis methods. The ALD method has advantages such as precise thickness control and conformal growth over a large area.\textsuperscript{18,28} In addition, most ALD processes are performed at low temperatures (<450 °C), which are favorable for device manufacturing schemes.\textsuperscript{29−31} Recently, interest in controlling the phase as well as the composition of metal-oxide-based materials has been made viable by ALD.\textsuperscript{32−54} Therefore, ALD could serve as an ideal technique for synthesizing both TMDs and TMTCs over a large area at low temperature with precise thickness control. Previously, TiS\textsubscript{2} has been reported to be synthesized by ALD using TiCl\textsubscript{4} and H\textsubscript{2}S with a growth per cycle (GPC) of 0.15 and 0.5 Å depending on the deposition temperature.\textsuperscript{16,17} Recently, ALD of amorphous TiS\textsubscript{3} has been reported by Nam et al.\textsuperscript{18} using tetraakis(dimethylamido)titanium and H\textsubscript{2}S at a deposition temperature between 120 and 180 °C with a GPC of ∼0.5 Å. They also reported the surface oxidation of TiS\textsubscript{3} after exposure to the ambient conditions. To the best of our knowledge, TiS\textsubscript{3} has not been synthesized by ALD.

This work describes a scalable, low-temperature ALD synthesis route with control over the phase of titanium sulfide (TiS\textsubscript{2}). The effect of varying the sulfur co-reactant and the deposition temperature on the phase of the deposited material is studied using an extensive array of characterization techniques (Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectrometry (RBS)).

Our work shows that ALD is well suited for obtaining both metallic TiS\textsubscript{2} and semiconducting TiS\textsubscript{3} in a temperature range of 100−200 °C. By tuning the temperature and the sulfur co-reactant in this temperature range, we demonstrate control over the phase.
99 B.V. Eindhoven, The Netherlands with a 2 MeV He\(^+\) beam source containing two detectors at scattering angles of 105 and 170°. Optical emission spectroscopy (OES) of the H\(_2\)S:Ar plasma was performed using a USB4000 spectrometer from Ocean Optics with a wavelength range of 180–1100 nm mounted vertically on top of the plasma source. Resistivity measurements were performed ex situ and at room temperature using a Signatone four-point probe in combination with a Keithley 2400 sourcemeter acting both as a current source and as a voltage meter. The resistivity of the thin films was determined from the slope of the \(I-V\) curve. The near-infrared (NIR) photoluminescence (PL) measurements were conducted using an inverted microscope in an epi-illumination geometry with an objective lens (50X Mitutoyo M Plan NIR Infinity Corrected, NA = 0.42) and a 2.040 eV excitation continuous wave laser. The PL spectra were recorded using an Andor Shamrock 163 spectrometer and an Andor iDus 1.7 μm InGaAs camera.

III. RESULTS AND DISCUSSION

Phase control between TiS\(_2\) and TiS\(_3\) during CVT has previously been observed to obey the following empirical relationship\(^{35}\)

\[
\log P_{(\text{Tor})} = 10.42(\pm 0.42) - 6850/T_{(K)}(\pm 340)
\]

where \(P\) corresponds to the partial pressure of sulfur and \(T\) corresponds to the synthesis/system temperature. This relationship indicates the sulfur partial pressure at which the pyrolysis of TiS\(_3\) to TiS\(_2\) is favored at a given temperature and therefore illustrates the minimum partial pressure of S required at a given temperature to synthesize TiS\(_3\). Thus, these two variables can be modulated accordingly to achieve phase control between TiS\(_2\) and TiS\(_3\). This forms the basis for studying both the effects of H\(_2\)S as a coreactant and the deposition temperature during the ALD process.
The effect of the coreactant sulfur species was studied by comparing H2S plasma (PE-ALD) and H2S gas (thermal ALD) as the coreactant at a deposition temperature of 100 °C for ∼30 nm thick TiSx thin films. The schematic representation of one complete ALD cycle as a function of time is shown in Figure 1a. In the case of PE-ALD, power was applied to the ICP source to ignite the plasma during the H2S:Ar coreactant step, as shown in Figure 1a, whereas in the case of thermal ALD the ICP source was turned off. The film thickness as a function of the number of ALD cycles as measured by in situ SE is shown in Figure 1b. The growth per cycle (GPC) was calculated by taking the slope of the linear region above 140 cycles; see Figure 1b. The atomic concentrations of O, C, and the S/Ti ratio were determined by RBS. The H content was determined by ERD. The resistivity was measured using a four-point probe method.

Table 1. In Situ SE, RBS, ERD, and Four-Point Probe Measurements of PE-ALD Deposited Titanium Sulfide Thin Film between 100 and 200 °C Deposition Temperatures

| Deposition Temperature (°C) | GPC, Å | S/Ti ratio | O, atom % | C, atom % | H, atom % | Resistivity, 10^9 μΩ cm |
|-----------------------------|--------|------------|-----------|-----------|-----------|------------------------|
| 100                         | 1.6    | 3.48 ± 0.02| 1.4 ± 0.6 | 3.7 ± 0.9 | 1.3 ± 0.1 | -                      |
| 150                         | 2.1    | 1.94 ± 0.01| 1.7 ± 0.1 | 1.0 ± 0.1 | 10.1 ± 0.8| 9                      |
| 200                         | 2.3    | 1.93 ± 0.01| 0.6 ± 0.1 | 0.6 ± 0.1 | 9.8 ± 0.8 | 3.5                    |

All films were ∼30 nm thick, and the GPC was calculated by taking the slope of the linear region above 140 cycles; see Figure 1b. The atomic concentrations of O, C, and the S/Ti ratio were determined by RBS. The H content was determined by ERD. The resistivity was measured using the four-point probe method.
of the H₂S:Ar plasma. In the H₂S:Ar plasma, S-containing species, including SH⁺ (at around 337 nm) and S₂ (peaks between 280 and 610 nm) species, were detected along with the Ar and H species. The contribution of S₂ species in the OES spectrum (between 280 and 610 nm) is significant (see Supporting Information Figure S2, where Figure 2 is compared with the OES spectrum of H₂Ar plasma without S species). In the case of thermal ALD, the H₂S:Ar gas (no optical emission in the gas phase) would most likely decompose into Ar and reactive H, SH, and S species at the reaction surface. By comparing both the cases, we hypothesize that the generation of S₂ species in the H₂S:Ar plasma could lead to the synthesis of TiS₂ [Ti₄(S₂)²S²⁺] where majority of the sulfur exists as S⁻S pairs. A similar observation was made by Carmalt et al. using CVD, where TiS₂ was synthesized only when a coreactant containing S₂ species was used. These S₂ species, however, are not present in the case of H₂S:Ar gas utilized during thermal ALD, which yielded only TiS₂.

Following the synthesis of TiS₂ by PE-ALD at 100 °C, the effect of the synthesis temperature (second variable in the earlier-mentioned empirical relationship) on the material’s phase/composition was studied by varying the deposition temperature in PE-ALD between 100 and 200 °C. In Figure 1b, the film thickness as a function of the number of ALD cycles is shown for the investigated deposition temperatures. Linear growth was observed for deposition at 100 °C without any nucleation delay, whereas for depositions at 150 and 200 °C, nonlinear growth was observed. This nonlinear growth can be ascribed to both the change in morphology of the film and the change in material phase (as will be discussed later). The GPC of the PE-ALD films increased from 1.6 Å at 100 °C to >2.0 Å at the higher temperatures; see Table 1. In comparison to the 100 °C film, the increase in GPC at higher temperatures is due to fin-like, out-of-plane oriented (OoPO) growth, as will be discussed later (in Figure 4). Similar growth behavior and increased GPC with OoPO growth have been previously observed for PE-ALD grown MoS₂.

Raman spectra of the films grown at higher temperatures were compared to the previously studied TiS₂ film grown at 100 °C. Figure 3a shows the Raman spectra of the films deposited at 150 and 200 °C containing two vibrational peaks at 230 and 330 cm⁻¹ along with a shoulder at 380 cm⁻¹ analogous to the Raman spectrum obtained for the TiS₂ film grown at 100 °C by thermal ALD (Figure 1e). These results demonstrate that phase control within the PE-ALD process was achieved between TiS₂ and TiS₃ by increasing the growth temperature, similar to CVT. In the PE-ALD process, the transition temperature of ~100 °C for TiS₂ to TiS₃ synthesis is very low in comparison to that in CVT (550 °C). Additionally, the XPS S 2p spectra for the 150 and 200 °C films corroborate this result with the Figure 1f. The S 2p spectra of both films display only one doublet at 161.1 and 162.3 eV (similar to thermal ALD grown films at 100 °C) corresponding to the spin–orbit doublet of S²⁻ species, indicating the deposition of TiS₂.

The valence band spectra of the films deposited by PE-ALD were also investigated using XPS analysis. The Fermi level (BE = 0 eV) was calibrated by measuring the Fermi edge of gold. At 100 °C, four broad peaks (see Figure 3b, black) at around 1.6, 4.5, 10.7, and 15.3 eV binding energies (BE) were observed. Due to the hybridization by S−S pairs in TiS₂, the two valence band peaks of TiS₂ split to form four broad peaks. The XPS valence band spectra for films deposited at 150 and 200 °C differed from the spectrum obtained at 100 °C showing only two broad peaks at around 3.5 and 13 eV (Figure 3b). In comparison to the literature, the spectra for the films deposited at 150 and 200 °C correspond to the valence band spectrum of TiS₂. These results further confirm that the phase-controlled synthesis of TiS₂/TiS₃ can be obtained by tuning the deposition temperature.

The composition and purity of the material were further determined using RBS measurements; see Table 1. The S/Ti ratio was measured to be 3.48 for the film deposited at 100 °C, whereas the S/Ti ratio for the films deposited at 150 and 200 °C was around 2 with a small S deficiency (or excess Ti). Additionally, contaminants such as C and O were detected within the error limit (Table 1), confirming the high purity of the films similar to the XPS measurements. Interestingly, ERD revealed a significant amount of H impurities (~10 atom %) for the 150 and 200 °C films. The H may have most likely been incorporated from the plasma coreactant and/or precursor ligands. It could be possible to reduce the H impurities in the film by further optimizing the H₂S:Ar plasma coreactant exposure time during the ALD cycle.

The crystallinity of the PE-ALD grown TiS₂ and TiS₃ films was investigated using grazing-incidence (GI)-XRD. The GI-XRD pattern of the film deposited at 100 °C (TiS₃) does not show well-defined peaks, indicating the formation of an amorphous film (Figure 3c). The films deposited at 150 and 200 °C, however, confirm the synthesis of crystalline 1T-TiS₂. The strong peak around 2θ of 15° corresponds to the (001) plane of 1T-TiS₂ and reveals a significant orientation.
This orientation effect can be explained by a crystalline layer in which a strong majority of crystals have their basal planes of 1T-TiS₂ oriented parallel to the substrate. This implies that below the OoPO structures visible in the SEM and TEM images (Figure 4) a continuous film of the aforementioned basal plane texture is present. The contribution of OoPO structures to the XRD pattern ((011) and (110) peaks) is small because of their limited volume fraction and random orientation with respect to the XRD detection geometry.

Additionally, the SAED pattern also shows the amorphous nature of the film synthesized at 100 °C (Figure 4g). Complementary to GI-XRD, the SAED patterns of the 150 and 200 °C films display reflections of lattice planes oriented perpendicular to the substrates. As a result, for both 150 and 200 °C films (Figure 4h,i) high-intensity (011), (110), and (010) rings are visible. The continuous nature of the rings confirms the polycrystalline nature of PE-ALD grown TiS₂ films. The discontinuous (001) ring reflects the presence of only a few OoPO structures per probed area having their c-axis parallel to the film surface.

Top-view SEM images (Figure 4a–c) display the morphology of the PE-ALD grown films deposited at all three temperatures. For the film deposited at 100 °C, no surface texture was observed. Similar to SEM, top-view TEM (Figure 4d) shows no lateral variation in the morphology (i.e., crystallinity and density) of the film. On the other hand, for the films deposited at 150 and 200 °C, top-view SEM images show OoPO structures, which can explain the high growth rate observed in the in situ SE measurements. Analogous OoPO structures have been observed previously for other TMDCs like MoS₂ and ReS₂. A similar relation between the OoPO film morphology and increased GPC has been previously observed for MoS₂. The top-view TEM images of films grown at 150 and 200 °C (Figure 4e,f) confirm the OoPO morphology of the TiS₂ film. The average distance between the 2D layers was measured to be ∼5.7 Å (Figure 4e,f), equivalent to the distance between two 1T-TiS₂ layers (Figure 1g).

The electrical resistivity of the PE-ALD deposited TiS₂ films was measured using a four-point probe method. The resistivity of the TiS₂ film deposited at 100 °C could not be measured due to its primarily amorphous nature, which could have yielded a high resistivity value that was beyond the measurement detection limit. Table 1 shows the measured resistivity of the other films. The deposited TiS₂ films exhibit a decrease in resistivity from 9000 to 3500 μΩ cm with the increase in temperature from 150 to 200 °C. From an application perspective, these low-resistivity 1T-TiS₂ films could be used as 2D contact materials with 2D semiconductors in device fabrication. (Note that the crystalline (by GI-XRD) TiS₂ film synthesized by thermal ALD at 100 °C has a resistivity of 2000 μΩ cm.) In summary, the effect of temperature on material composition, phase, morphology, and resistivity was studied in detail. All of the discussed characterization techniques confirm the synthesis of TiS₃ at 100 °C and a transition to TiS₂ at temperatures above 100 °C by PE-ALD. We also investigated the effect of deposition temperature by thermal ALD and observed no change in phase from TiS₂ at all investigated temperatures. These studies, however, will be discussed in detail in a future work.

The crystallinity of the PE-ALD grown amorphous TiS₃ film at 100 °C deposition temperature was improved by a postdeposition annealing step. To avoid oxidation to TiO₂ and pyrolysis to TiS₂ during annealing, a sulfur-rich atmosphere was chosen for the annealing treatment of 3 h at 400 °C. The Raman spectra of TiS₃ before and after annealing are compared in Figure 5a. The four vibration peaks observed for the annealed film confirm that the TiS₃ phase was preserved. Additionally, the red shift of the vibration peaks along with the reduced width of the peaks, indicated improved crystallinity of the film. Some surface oxidation to anatase TiO₂ (∼143 cm⁻¹) was observed, probably due to the transfer of the sample through the air from the ALD chamber after deposition to the annealing furnace. The GI-XRD pattern (Figure 5b) of the annealed film also confirmed improved crystallinity and preservation of the TiS₃ phase of the film, along with TiO₂ (*) due to surface oxidation. Similar to the PE-ALD grown 1T-TiS₂ crystalline films, a strong peak around 2θ of 10° corresponds to the (001) plane of TiS₂ and indicates that basal planes of TiS₃ are oriented parallel to the substrate. An average (vertical) crystal size of ∼16 nm was calculated using the Scherrer equation.

A cross-sectional TEM image of the postdeposition annealed TiS₃ film displays the layered crystalline nature of the postdeposition annealed TiS₃ film (Figure 5c). Similar to the results from GI-XRD, the basal planes of TiS₃ are oriented parallel to the substrate. An average (lateral) crystal size of ∼50 nm was measured from the cross-sectional TEM images. The corresponding EDX elemental mapping of the S, Ti, and O are shown in Figure 5d–f, respectively. EDX mapping also further confirms the surface oxidation (to TiO₂) of the film and also
We report on a low-temperature ALD process with which the phase of titanium sulfide films can be precisely tuned between TiS$_2$ and TiS$_3$. The key to successful phase control was to carefully tune the coreactant composition and deposition temperature. The generation of S$_2$ species in the H$_2$S plasma is highlighted in the interface between TiO$_2$ and TiS$_3$. Figure 5g shows a high-resolution HAADF-STEM image of a cross-sectional region in the postdeposition annealed film with atomic resolution. The average measured distance between two TiS$_3$ layers reported in the literature.$^{46}$ In the zoomed-in inset (Figure 5h), an overlay of the TiS$_3$ crystal structure viewed along the [010] zone axis, is shown in the HAADF-STEM image.

Finally, the semiconducting nature of the TiS$_3$ after annealing was confirmed using NIR PL spectroscopy. PL was observed to be centered around ~1400 nm ($\sim$0.9 eV) after annealing (Figure 5i), whereas it was not detectable before annealing. The position of the PL peak is close to the band gap of TiS$_3$, $^{47,48}$ Thus, the postdeposition annealing treatment of the PE-ALD grown amorphous TiS$_3$ at 400 °C improves the quality and crystallinity of the TiS$_3$ film.

IV. CONCLUSIONS

We report on a low-temperature ALD process with which the phase of titanium sulfide films can be precisely tuned between TiS$_2$ and TiS$_3$. The key to successful phase control was to carefultly tune the coreactant composition and deposition temperature. The generation of S$_2$ species in the H$_2$S plasma has been speculated to lead to the formation of amorphous TiS$_3$ by PE-ALD at a deposition temperature of 100 °C. Above 100 °C, a transition to the formation of TiS$_2$ occurs by PE-ALD. Electrical measurements show the low resistive nature of the TiS$_3$ films. The crystallinity of PE-ALD grown TiS$_3$ films was improved by adding a postdeposition annealing step of 400 °C for 3 h. After annealing, NIR PL was observed at ~1400 nm, confirming the direct optical band gap of TiS$_3$ at ~0.9 eV. This approach can potentially be extended to other transition-metal di- and tri-chalcogenides, opening up new avenues for implementation of both transition-metal di- and tri-chalcogenides in nano- and optoelectronic device fabrication schemes.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b02895.

Information about both thermal and PE-ALD saturation curves measured using in situ SE and additional details comparing OES spectra of H$_2$S:Ar plasma with that of H$_2$:Ar plasma (PDF)

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**Notes**

The authors declare no competing financial interest.

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