The conversion mechanism of amorphous silicon to stoichiometric WS₂

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The deposition of ultra-thin tungsten films and their related 2D chalcogen compounds on large area dielectric substrates by gas phase reactions is challenging. The lack of nucleation sites complicates the adsorption of W-related precursors and subsequent sulfurization usually requires high temperatures. We propose here a technique in which a thin solid amorphous silicon film is used as reductant for the gas phase precursor WF₆ leading to the conversion to metallic W. The selectivity of the W conversion towards the underlying dielectric surfaces is demonstrated. The role of the Si surface preparation, the conversion temperature, and Si thickness on the formation process is investigated. Further, the in situ conversion of the metallic tungsten into thin stoichiometric WS₂ is achieved by a cyclic approach based on WF₆ and H₂S pulses at the moderate temperature of 450 °C, which is much lower than usual oxide sulfurization processes.

Introduction

Ultra-thin semiconducting atomic layers such as the transition-metal dichalcogenides (TMDs) WS₂ or MoS₂ show specific properties due to their reduced dimensionality. Monolayers of these TMDs reveal sulfur-terminated basal planes and multilayers are bonded by van der Waals forces, hence, their ideal surface is free of dangling bonds.² Due to their lower relative permittivity in comparison to Si, they are also predicted to be more resistant against short-channel effects in field effect transistors and are promising for future scaling in nanoelectronics.² Besides this, these materials are promising building blocks in optoelectronics, spintronics, and flexible electronics.³⁻⁵ In recent years, much progress on the growth of MX₂ materials has been reported, especially for MoS₂. In comparison to MoS₂, the TMD WS₂ received less attention, despite its higher predicted phonon-limited electron mobility of 700 cm² V⁻¹ s⁻¹ in monolayer due to its lower effective charge carrier mass, in comparison to the value of 440 cm² V⁻¹ s⁻¹ reported for MoS₂.⁶⁻⁸ Those theoretical performances are smaller in real devices due to structural defects such as grain boundaries and sulfur vacancies, which are occurring as a result of the growth process or post treatment.⁹,¹⁰

A common approach for deposition on large areas is the chemical vapor deposition (CVD) by evaporation of MoO₃ and S supported by Ar/H₂ flow in furnaces with different temperature zones.¹¹⁻¹³ This allows the deposition of monolayer triangles with lateral dimensions of a few tens of micron. The crystal orientation can be controlled by using crystalline guiding substrates such as sapphire wafers or GaN films.¹⁴⁻¹⁷ Besides of MoO₃, metal halides have been used for deposition as well, since their boiling points are smaller than for the oxides and hence, their vapor transport into processing reactors to the substrate surface is facilitated.¹⁸⁻²⁰ The transition-metal chlorides can be evaporated already below 300 °C and the fluorides are even volatile at room temperature. Besides metal halides, also volatile metal–organic precursors are used to deposit thin films.²¹⁻²⁴ Those CVD methods can yield large MX₂ grains, if the nucleation starts from one nucleation point and extends laterally to form the characteristic triangles. Next to the CVD methods, also conversion reactions have been widely investigated. In such reactions, pre-deposited metallic or metal-oxide layers are sulfurized in evaporated elemental sulfur or H₂S.²⁵ However, sulfurization results in much smaller grain size than CVD for a given temperature, since sulfurized films are initially nanocrystalline and need high recrystallization temperatures to enable grain boundary migration.

The majority of studies were done for MoS₂ due to the ease of fabrication by co-evaporation of MoO₃ (melting point at 795 °C) and sulfur in tube furnaces and the MoS₂ deposition directly from the gas phase.⁶,⁸ However, WO₃ needed for WS₂ has a high bond energy and sublimes at temperatures higher
than 900 °C, which is less practical than MoO 3 . Song et al. deposited thin WO 3 films by ALD at 300 °C and sulfurized these films afterwards at 1000 °C. However, the sulfurization of WO 3 requires those high temperatures to enable the oxygen–sulfur exchange reaction in this oxide with high bond energy. We studied in this work an alternative approach, in which the tungsten is sulfurized directly from the metallic state. Normally, a metallic layer is difficult to maintain during the transport of a substrate in air. Therefore, the deposition is done in situ in one reactor without vacuum break to avoid oxidation. In this paper we elaborate on the process described earlier, in which we convert an amorphous silicon film by WF 6 into metallic W and convert it in situ into WS 2 at a moderate processing temperature of 450 °C in H 2 S. This study discusses the detailed observations of the formation mechanisms, namely the Si-to-W conversion and the sulfurization directly from metallic W to WS 2 . The necessity for the surface preparation and restrictions with regards to thickness control, temperature, and structure are discussed.

The selective deposition of W on Si surfaces by CVD is a well-known process, which is mainly used for W-plug formation in vertical interconnect accesses (VIA) in combination with a Ti buffer layer. In contrast, the W deposition on dielectric surfaces is more challenging due to the lack of potential nucleation sites. The formation of a thin W film from the precursor WF 6 on dielectrics such as Al 2 O 3 , HfO 2 , or SiN requires the use of a reductant, since these dielectrics do not provide chemisorption sites for the precursor. Successful nucleation could be achieved by the use of H 2 plasma or gases like SiH 4 , SiH 3 , B 2 H 6 , GeH 4 , or solids like elemental Si. The aforementioned gaseous precursors are used for ALD processes to achieve layer-by-layer deposition of amorphous or polycrystalline films. However, they deposit the target material on the whole substrate and not in specific regions. Nonetheless, a solid precursor like a thin Si film can be pre-patterned and controls the areas for the conversion.

In contrast to the above described methods, the technique developed in this paper allows the selective deposition of WS 2 with arbitrary thickness equivalent to multilayer thickness down to a monolayer over wafer sizes of 300 mm diameter and exploits conventional tools for CMOS fabrication such as physical vapor deposition (PVD), wet chemical processing, and CVD. Here we provide insight into the conversion mechanisms with a focus on surface preparation, conversion temperature, and thickness correlation.

This conversion process can be used in combination with advanced techniques such as atomic layer etching (ALEt) to form selectively grown patterns on sensitive underlying films bringing advanced Beyond Si-CMOS concepts, such as tunnel field-effect transistors (TFET) or spintronic devices a step closer.

**Methods**

Substrates used in this work were 300 mm Si wafers coated with a 20 nm-thick thermally grown SiO 2 layer to provide interference contrast for 2D material visibility. This SiO 2 was covered by an atomic layer-deposited (ALD) Al 2 O 3 and crystallized in O 2 -rich environment at 1000 °C to chemically mimic a sapphire surface and to protect the Si wafer from reactions with the used gas phase precursor or wet-chemical surface preparations.

Amorphous silicon layers were deposited by PVD with a low deposition rate of 6.8 Å min⁻¹. This amorphous silicon is a uniform, sacrificial layer and used as reductant, i.e., it is consumed during the proceeding steps. The native SiO 2 was removed and Si was H-passivated by a 20 s long 0.5% HF rinse and followed by an extensive H 2 O rinse. These layers were immediately exposed to alternating gas pulses of WF 6 and H 2 S in a CVD reactor at a temperature of 450 °C according to the scheme shown in Fig. 1.

This converted the Si film into metallic W and subsequently into WS 2 . The 15 s long gas pulses were separated by N 2 purges. The pressure was kept constant at 266 Pa. The conversion mechanism was thoroughly analyzed by Rutherford backscattering spectrometry (RBS) using 1.523 MeV He⁺ particles. Raman spectra were measured by a Horiba LabRAM HR with 532 nm excitation wavelength and a grating of 1800 grooves per mm. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) spectra were acquired with a Thermofinstruments Theta300 system using a monochromatized Al Kα X-ray source (1486.6 eV) and all spectra were integrated over their measurement angles to obtain a high signal-to-noise ratio. Atomic force microscopy (AFM) by a Bruker Dimension ICON PT was used in tapping mode to collect information about the surface roughness. Selected samples were coated with spin-on-carbon (SOC) and cut with a 5 kV Ga⁺ focused ion beam (FIB) into transmission-electron microscopy (TEM) specimens and then observed by a FEI Titan3 G2 60–300 with a Super-X EDS detector system. Grazing incidence X-ray diffraction spectra were recorded by a Panalytical XPert Pro MPD using an incidence angle of 1°.

**Results and discussion**

The deposition of WS 2 from gas phase precursors proceeds in two steps, the Si conversion to ultrathin, metallic W layers and the sulfurization of those metallic layers to WS 2 . The following
section discusses the impact of surface oxidation and the requirements for the Si surface preparation and the quantification of the conversion process from Si to W. Afterwards, the sulfurization and its constraints with respect to penetration depth and temperature are explained. After analyzing both processes separately, the combination was optimized to obtain stoichiometric films on an insulating substrate.

**Redox reactions based on Si, WF$_6$, and H$_2$S**

**Si conversion to W: role of surface passivation.** Depending on the temperature, gaseous WF$_6$ reacts with Si according to the following paths by the up-diffusion of Si through thin W and reaction with the gaseous precursor at the surface:41

At 400°C: $3\text{Si}(s) + 2\text{WF}_6(g) \rightleftharpoons 2\text{W}(s) + 3\text{SiF}_4(g)$ \hspace{1cm} (1.1)

or

at 700°C: $3\text{Si}(s) + \text{WF}_6(g) \rightleftharpoons \text{W}(s) + 3\text{SiF}_2(g)$. \hspace{1cm} (1.2)

Wafers with 7.5 Å-thick Si were exposed to the WF$_6$ at 450°C after different periods upon Si deposition and the deposited W amount was quantified by RBS. The expected value for the number of W atoms per area $N_{W}/A$ in the case of full conversion was calculated by

$$N_{W} = \frac{x \cdot N_{Si}}{A} = \frac{x \cdot \rho_{Si} \cdot A_{Si} \cdot t_{Si}}{3 \cdot M_{Si}} \hspace{1cm} (1.3)$$

with the reaction coefficient $x$ for W (either 2 or 1 for eqn (1.1) or (1.2), respectively), the pre-deposited Si thickness $t_{Si}$ and the corresponding number of Si atoms per area $N_{Si}/A$. The amorphous Si density $\rho_{Si}$ can vary between 1.7 and 2.3 g cm$^{-3}$ depending on the deposition conditions.42 With the molar mass $M_{Si}$ the theoretical density of W after full conversion for reaction (1.1) is in the range of $1.83 \times 10^{15}$ to $2.47 \times 10^{15}$ at per cm$^2$ and for reaction (1.2) it would yield only between $0.91 \times 10^{15}$ and $1.23 \times 10^{15}$ at per cm$^2$. Experimentally the 7.5 Å Si after conversion yielded $2.47 \times 10^{15}$ at per cm$^2$. This confirms that reaction (1.1) with the coefficient $x = 2$ occurred and the Si density of the pre deposited Si of silicon is similar to the crystalline density.

However, this amount was only achieved when the conversion with WF$_6$ was done immediately after the Si deposition. With increasing delay between the Si deposition and the conversion, less Si was converted to W for a similar Si amount, as shown in Fig. 2. This is related to the formation of native SiO$_2$, of which the thickness is time-dependent.

The amorphous Si forms a native oxide in air of a few Å. The exact thickness of this native oxide depends on the residence time in air.43 Upon immediate WF$_6$ exposure for $t_{WF6} = 15$ s, the nominal Si amount of 7.5 Å resulted in nearly full conversion, whereas after 30 min only 55% of the expected value was observed, after 24 h only 43%, and upon two weeks delay, the deposited W amount was only 2% of the expected value of full conversion.

This reveals the decreasing efficiency of Si-to-W conversion with increasing air exposure time. This observation can be explained by the non-reactivity of WF$_6$ and SiO$_2$ at the processing temperature of 450°C.44 It is therefore essential to carefully control the native oxide growth to avoid variability in W deposition. Samples treated with 14 cycles starting with $t_{WF6} = 15$ s WF$_6$ exposure but 24 h after Si deposition, show residual Si–O in the converted film according to XPS (Fig. 3a), confirming the strongly limited reactivity of SiO$_2$ with WF$_6$. The SiO$_2$ is represented as the high energetic peak in the Si 2p spectra. In contrast to this, elemental Si being located at lower binding energy could not be quantified and only noise level was detected in this part of the spectrum, hence all elemental Si was consumed in the conversion process. Correspondingly, reaction (1.1) occurred even through a thin native SiO$_2$ layer, which is not fully closed yet after short delay.

Further analysis of the XPS spectra shown in Fig. 3b revealed that oxygen was incorporated in the deposited W-compound. The spectrum shows two doublets of the W 4f peak: the lower energetic doublet is related to the W–S bonds, thus it represents the IV+ oxidation state of W, which is typically related to WS$_2$.45,46 At higher binding energy, there is the W 4f doublet for WO$_3$ – this corresponds to W in the VI+ oxidation state. This doublet is superimposed to the W 5p peak at the binding energy at 39.5 eV in this spectrum. The oxide can be distinguished qualitatively from the pure compound by the evolving shoulder next to the WS$_2$ doublet, which is part of the oxide characteristic doublet.

The quantitative oxide fraction of the deposited film was 16% for the immediate conversion and 19% for the conversion after 24 h (only partially converted). Both observations show higher oxidation than the typical 10–12% oxidation (full conversion) we observe for the best material, probably originating from minor air oxidation. Typically, S-saturated W atoms oxidize only slowly under dry conditions and are stable for short-term as long as no elevated temperatures or moisture is applied for longer time.47 The observed WO$_3$ oxidation implies that another oxygen source is present.

To identify this source, the composition was further analyzed upon deposition. The spectra in Fig. 3b reveal a higher
oxidation level in the film converted after 24 h in comparison to the one which was immediately converted. In addition, GIXRD spectra acquired upon deposition (Fig. 3c) revealed significant peaks at 16.5° and 25.4° being characteristic for tungstite, WO₃·H₂O. This implies that the reaction product results from the interaction of SiO₂, WF₆, and air environment upon processing. SiO₂ cannot be directly etched by WF₆ due to its selectivity. However, WF₆ reacts with Si by penetrating through pinholes in the not fully closed native oxide layer, if this is still thin when it is only a few hours old. This forms SiF₄ as byproduct according to reaction (1.1), leading to the formation of a volatile silicon oxyfluoride according to (1.4):⁴⁹

\[
3\text{SiF}_4(g) + \text{SiO}_2(s) \rightleftharpoons 2\text{Si}_2\text{OF}_6(g) \tag{1.4}
\]

The O-containing reaction product from (1.4) is detracted by further reaction with WF₆ in the gas phase forming the metal-oxide compound according to the exergonic reaction \(\Delta G = -300 \text{ kJ mol}^{-1}\):

\[
3\text{Si}_2\text{OF}_6(g) + \text{WF}_6(g) \rightleftharpoons \text{WO}_3 + 6\text{SiF}_4(g) \tag{1.5}
\]

The oxygen of Si₂OF₆ could react with WF₆ due to the high affinity between both according to reaction (1.5). Upon air exposure, the incorporated oxide can hydrate and form the tungstite as evidenced in Fig. 3c. To avoid the formation of tungstite and to achieve pure, oxygen-free WS₂, the incorporation of any oxygen on the sample surface has to be avoided. The challenges of preparing an O-free surface are twofold: on the one hand, the oxide regrowth on deposited Si is time-dependent and hence, it can vary depending on the time between Si deposition and oxide removal. As a result, the amount of elemental Si left is also time-dependent. On the other hand, the oxide regrowth should be avoided to minimize the adsorption of O₂ or H₂O prior to the W-compound deposition step. To tackle the first challenge of time-dependent oxidation, a chemical oxide based on ozonated H₂O was grown on the Si surface to achieve repeatable, constant Si consumption.⁵⁰ Afterwards, 0.5% HF was applied for 200 s to remove the native/chemical oxide and then followed by an extensive H₂O rinse to passivate the surface with hydrogen, resulting in a hydrophobic surface that remains stable for extended periods of time.⁵¹

As the GIXRD spectra in Fig. 3d show, the tungstite peaks are absent for the samples, which received the treatment of chemical oxidation and HF before the conversion process and only tungstenite is visible at 14°. Additionally, the XPS spectra in Fig. 3b reveal that the WO₃-related doublet diminishes and only the W 5f peak at high binding energy remains. According to the XPS quantification procedure, the remaining oxidation level of W-bonds is 12%, which is the lowest value we obtain for any 2D material grown in our laboratory and that we could measure by ex situ analysis. By combination of ozonation and HF treatment the surface oxide can be controlled and removed in a reproducible way leading to a stable H-passivated Si which can be used as a vehicle to study the conversion mechanism.

This conversion reaction was described earlier for W CVD deposition by the upward diffusion of Si through the growing W layer.⁴¹ The segregated Si on top can react with the gaseous precursor, forms volatile SiF₄, and deposits the metallic W layer.

The film was exposed to 3 s WF₆ and a W amount of \(2.5 \times 10^{15}\) at per cm² was achieved. Saturation was observed after 15 s exposure as can be seen from Fig. 4a. The XPS spectra in Fig. 4b show remaining elemental Si and SiO₂ after the unsaturated 3 s WF₆ pulse and a Si-free surface for larger doses. This means that the dose for 3 s was too small to convert all the Si, whereas the 15 s are sufficient for converting all Si into W without any residual Si or SiO₂ incorporated.

Afterwards Si layers with different thicknesses were prepared and converted to W. The linear relationship between the
deposited W amount and the pre-deposited Si is depicted in Fig. 5. The intersection with the abscissa (1 nm) represents the amount of silicon which was consumed during the O3/H2O oxidation and the HF-based SiO2 removal. The slope derived from the linear fit is 2.51 \times 10^{15} \text{ at per cm}^2 \text{ per nm.}

The linear correlation between W and Si and the absence of any residual Si (Fig. 2b) demonstrate the complete conversion of Si into W at 450 \text{ C} and in this way allows a precise controllability of the deposited amount.

WF6 does not react with the crystallized Al2O3 underlayer as long as no other reductant is provided illustrating that this Si-to-W conversion process is selective as demonstrated in an earlier paper.30

**Sulfurization reaction for the conversion of W to WS2.** After determining the parameters for a complete conversion of the pre-deposited Si amount, the parameters of the sulfurization pulse were studied to obtain a stoichiometric WS2. Obviously, this sulfurization pulse was applied in situ to avoid air exposure of the formed metallic compound, since it would oxidize rapidly.52

The H2S pulse converts the deposited material according to:

\[
W(s) + 2H2S(g) \rightleftharpoons WS2(s) + 4H2(g) \quad (1.6)
\]

We can assume that all the initially deposited tungsten is in the metallic state, since the H2S pulse is applied in situ and no O2 is involved in any of the reactions after cleaning the surface properly. After a t_{H2S} = 15 s H2S pulse at 450 \text{ C}, the sulfurization yielded only a S/W ratio of 1.3, hence the film was non-stoichiometric and only 75\% of the maximum sulfur amount was reached since the sulfurization reaction was not complete. A second cycle being equivalent to a dose for 30 s already increased the ratio to 1.7. Adding twelve more cycles with a total H2S dosing of 210 s resulted in a S/W ratio of 1.8 and saturated around this level for a given initial Si thickness. This was equivalent to 90\% of the total theoretical sulfur amount.

**Influence of the processing temperature.** According to Fig. 5, an initial Si thickness of 3 nm is necessary to realize a multilayer structure of four layers of WS2. For this thickness, the temperature window was investigated. Fig. 6a shows the S/W ratio after formation at various temperatures between 325 \text{ C} and 450 \text{ C}. With increasing temperature, the incorporated S amount is increasing as well and is reaching a S/W ratio close to 2 for 450 \text{ C}, but the W amount was constant for all three temperatures. The XPS spectra in Fig. 6b show decreasing WO3 doublets for increasing deposition temperatures, before reaching a minimum for 450 \text{ C}. We interpret the W–O oxide formation as saturation of metallic bonds upon air exposure, which is a different effect than shown before which was the oxide formation due to an oxide-contaminated surface of the Si precursor. When the sulfurization is conducted at 450 \text{ C}, a higher fraction of W is sulfurized and all the accessible W atoms are saturated with sulfur, so that the material is inert against spontaneous oxidation in air. For T < 450 \text{ C}, the W films are not completely sulfurized and remaining W atoms oxidize in air.

The Raman spectra in Fig. 6c show the characteristic peaks for WS2: the higher the temperature, the higher are the intensities of the 2LA(M)/E12g and A1g peaks.33 The overlapping peaks 2LA(M) and E12g describe the second order Raman resonance peak of the longitudinal acoustic mode and the in-plane vibrational modes, respectively. The A1g peaks describe the out-of-plane
vibrational modes of the W–S bonds. Note how in contrast, the intensity of the Si 2TA mode at 300 cm$^{-1}$ coming from the substrate remains relatively constant. Together with the rising LA(M) mode, often referred to as a measure for the disorder in MX$_2$ films, this can be interpreted as an increase in the WS$_2$ amount.\textsuperscript{54}

These observations show that for $T \geq 325$ °C, the limiting step is the sulfurization. For a given temperature, sufficiently long dosing of H$_2$S had to be provided to convert the thickness of a four layer-equivalent film. This is due to the diffusion of the reactant H$_2$S through the top layer of WS$_x$ and the out-diffusion of the reaction product H$_2$ according to reaction (1.6). Diffusion is a temperature-determined process and thus, higher temperatures allow deeper diffusion of sulfur for a given reaction time.

At 450 °C the conversion of a 3 nm-thick Si and the stoichiometric sulfurization of the W could be achieved. This temperature was used in all the following experiments to obtain stoichiometric films.

Influence of the starting Si thickness for controllability of layers. The properties of 2D materials vary significantly with the thickness and the optimal thickness for MX$_2$ transistors remains under debate.\textsuperscript{55,56} In the following we evaluated whether the WS$_2$ thickness could be modulated by the amount of pre deposited Si.

To achieve the deposition of different thicknesses of stoichiometric WS$_2$ films, Si films with different thicknesses were pre deposited and converted to WS$_2$ with $t_{WF_6} = t_{H_2S} = 15$ s long pulses at 450 °C. The amount of W and S was quantified as shown in Fig. 5.

While the W amount increases linearly with the amount of pre deposited Si, the S amount increases linearly up to $\sim 3.75$ nm Si and then saturates, there is no more sulfur incorporation above this amount. This is related to the limited H$_2$S diffusion into the deposited film at the temperature used.\textsuperscript{55,57} Since the conversion Si $\rightarrow$ W is done \textit{in situ} with the H$_2$S sulfurization, both cycles are conducted at the same temperature. H$_2$S has to penetrate through the surface layer, react with the metal underneath, and H$_2$ as reaction product has to diffuse out of the films. The 450 °C process is capable of sulfurizing one to six layers at the given H$_2$S dose and temperature. If the films become too thick, the H$_2$S is not capable of diffusing deep enough, which can be seen by residual metallic W in the XPS spectra in Fig. 7. There is also an increased WO$_3$ amount appearing, being buried at the interface between the sulfur-terminated W–S and the metallic W. This WO$_3$ is formed due to non-reacted W, which is brought into contact with O$_2$ from the atmosphere. Hence, at room temperature O$_2$ can still diffuse through the top layer oxidizing a part of the metallic W underneath, which can be understood from the smaller van der Waals radius of oxygen of 1.52 Å with respect to the larger one of sulfur with 1.80 Å. Thus, O$_2$ is assumed to penetrate deeper than H$_2$S at low temperatures. Diffusion is a temperature-controlled mechanism, therefore only higher temperatures or longer annealing periods could sulfurize thicker layers, but this is out of the range of the available experimental setup and also not targeted for the application in few-layered active films.

Necessity of a cycled process. Introducing the gas pulses sequentially with a saturated WF$_6$ pulse for conversion and at least partial sulfurization is essential due to the interaction of the solid and gas compounds. We tested the hypothesis whether a partial conversion by a short WF$_6$ pulse, followed
by a long sulfurization step could result in smaller nucleation density and facilitate large crystal growth from fewer nuclei by repeating such cycles. However, we observed that after the first unsaturated WF$_6$ pulse and the H$_2$S pulse, no further conversion of Si into W occurred after the second WF$_6$ cycle, as WF$_6$ cannot reach the elemental Si underneath anymore and the Si does not diffuse upward through the WS$_2$. In contrast, the sulfuration reaction continues in the second cycle. Hence the formed WS$_2$ top layer act as a barrier and prevents the further upward diffusion of Si through the WS$_2$ film and the Si interaction with WF$_6$.

The simultaneous injection of WF$_6$ and H$_2$S was investigated on the H-terminated Si (CVD regime). We observed the formation of a film with monolayer-equivalent thickness being also stoichiometric. However, the thickness of this film did not scale with deposition time. In this case the surface reaction took place as well, but further surface reaction was strongly reduced and formation of a second layer occurred only very slowly, since the top surface WS$_2$ film prevented any further exchange between the buried reductant silicon and the gaseous WF$_6$.

The goal of this work is the deposition of TMD on the insulating substrate without leaving silicon traces behind. We conclude that it is necessary to first fully convert the Si into W, and only afterwards the sulfurization of the W film can be carried out.

Fig. 8 shows a TEM cross-sectional image of a stoichiometric film deposited with optimized conditions. The image shows in the bottom part the polycrystalline Al$_2$O$_3$, in the middle the WS$_2$ films, and above the spin-on-carbon (SOC) capping layer. In the SOC layer some darker regions are visible, which represents driven-out sulfur by the sample preparation through focussed ion beam.

The layered structure of the W and S is visible, but with short-range order. The size of clusters with parallel basal plane structure is less than 3 nm and, in between, areas appear amorphous. The similar random orientation of WS$_2$ clusters was observed for different thicknesses and similar stoichiometry of the films. In case of thin non-stoichiometric films, the basal planes of the clusters are rather vertically aligned and WO$_3$ clusters remain in the film. The stoichiometric films can be used for further recrystallization experiments, which is part of further research.$^{58,59}$

Conclusions

A method has been described, allowing to deposit one to six layers WS$_2$. The method starts from an amorphous Si, of which the thickness determines the amount of WS$_2$ to be formed. To obtain pure WS$_2$, the Si layer needs to be oxygen-free. Reproducible Si layers can be obtained by the oxidation with a H$_2$O-O$_3$ mixture and a subsequent HF treatment, which passivates the surface with H and delays re-oxidation. The silicon layers can be converted to metallic W with WF$_6$ at $T \geq 325~{^\circ}C$, then in situ sulfurized by H$_2$S, which is energetically favorable over oxygen–sulfur exchange in WO$_3$ compounds. The formation of WS$_2$ creates a barrier against a subsequent SiWF$_6$ exchange, which imposes that the starting Si film must be fully converted into W in the first cycle. The sulfurization step is a diffusion-driven process and is limited to a thickness equivalent of six layers WS$_2$ at 450 °C. The obtained WS$_2$ layers with random basal plane orientation can serve as template for subsequent recrystallization to obtain larger crystals. We believe that this technique can pave the way for a selective deposition on large substrates and could enable heterostructures for TFETs, spintronics, and optical applications.

Conflicts of interest

There are no conflicts to declare.

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References

7 K. Chen and S. Chang, Phonon limited electron mobility calculation of transition metal dichalcogenide monolayer,


44. A. Kepten, Studies of the Possible Reaction of WF6 with SiO2 and Si3N4 at Several Temperatures, *J. Electrochem. Soc.*, 1992, **139**(8), 2331.


